

Novel Catalysts for the Selective Hydration of Ethylene Oxide (EO) to Ethylene Glycol (MEG)

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Introduction

Most of the 15 million metric tons of MEG is produced by the non-catalytic or thermal hydration of ethylene oxide in water [1]. Despite using a large excess of water, about 10 % by-product (by weight) of lower value (per ton) DEG (di-ethylene glycol) is produced [2]. To maximize the MEG production, many different catalysts as well as new production methods such as reactive distillation have been reported. Shell and Mitsubishi's recently announced OMEGA (Only MEG Advance) process, where EO is reacted with CO₂ to form ethylene carbonate which is then hydrolyzed to MEG, is one of the more successful approaches [3].

The major drawback of the known one-step catalytic process is lack of catalyst stability. Catalysts based on metal anions (i.e. MoO₄²⁻) reportedly leach metal and those based on HCO₃⁻ swell over time[4]. New catalysts are therefore desired. We have used a Multiclave™ to rapidly screen several different classes of potential catalysts. We report the results of this screening in this presentation.

Materials and Methods

Chemicals were used as received from commercial sources or were prepared by literature methods. The potential catalysts were weighed into a cell of the multiclave and dissolved in water. A 4:1 (w) water/EO mixture was added at 100 °C using a pump, a stream selector valve and a timer. The mixture was kept at 100 °C for 10 hours to ensure complete conversion. The selectivity was determined by GC and compared to a blank reaction without catalyst.

Results and Discussion

We have screened three classes of compounds as potential catalysts; amines (in the presence of CO₂), bi-functional (such as EDTA type compounds) and SALEN type compounds. The use of tertiary amine compounds in the presence of CO₂ is known.[5] We have found that even primary amines such as ethylene diamine show high selectivity for the catalytic hydration of EO to MEG. The selectivity appears to correlate to the pK_a of the base.

The hydration of EO to MEG is both acid and base catalyzed.[6] We speculated that the concurrent use of an acid and base could yield an effective catalyst. The use of a buffer of the acid and conjugate base has been reported.[7] In this case, the selectivity correlated well to the apparent pH of the solution used for the catalysis.

The use of SALEN type compounds is known for the kinetic resolution of racemic epoxides by hydration with water.[8] The high yield of the glycol in this reaction led us to try these type of compounds. We have found the JACOBSEN's catalyst is active even at room temperature with selectivities as high as 97 % to MEG. This reaction is usually run in the presence of some acid, usually acetic. We have found that just the ligand in the presence of acetic acid is also an effective catalyst. The use of the ligand in the presence of CO₂ is also effective. Presented in Table 1 are selected compounds of each of the three classes investigated.

Table 1. Selected Catalysts found by screening with the multiclave™.

Catalyst System	Selectivity to MEG
1,4-diaza bicyclo[2,2,2]octane (DABCO), pK _a 8.82, CO ₂	96
1,3-diaminopropane (DAP), pK _a 10.65, CO ₂	96
NaEDTA, pH 4	89
N,N'-bis(salicylidene)ethylenediamine, CO ₂	93
N,N'-bis(salicylidene)ethylenediamine, w 4 eq acetic acid	95
JACOBSEN's catalyst, RT	97
Thermal (no catalyst). (w CO ₂)	83, 88

Significance

We have demonstrated the efficacy of using the MULTICLAVE™ for the rapid screening of potential catalysts for the hydration of EO to MEG. We have found three different novel classes of catalysts for this reaction.

References

1. Lacson, J. "Ethylene Glycols", in Chemical Economics Handbook, SRI International, 2003.
2. PERP Report, Ethylene Oxide/Ethylene Glycol, NEXANT Chem Systems, 04/05-5, 2006
3. Shell Magazine, Spring 2006, web edition: <http://www.shellchemicals.com/magazine>
4. Shvets, V. F.; Kozlovskiy, R. A.; Kozlovskiy, I. A.; Makarov, M. G.; Suchkov, J. P.; Koustov, A. V., *Chem. Eng. J.* 107, 199 (2005)
5. Cipriani, G., Neri, C., Romano, U., US Patent 4,307,256 (1981).
6. Isaac, N.S., in "Physical Organic Chemistry" p. 330. John Wiley & Sons, New York, 1987.
7. T. Masuda, K. Asano, N. Hori, S. Ando, U.S. Patent 4,937,393 (1990).
8. Jacobsen, E.N. *Acc. Chem. Res.* 33, 421 (2000).