Hydration of epoxide on Co(salen)-based molecular catalysts

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Abstract: 1,2-propylene glycol (PG) is an important bulk chemical, yet the method for producing PG in industry by non-catalytic hydration of propylene oxide (PO) under high molar ratio of water to PO is of high-energy-consumption. Up to date, various catalysts have been developed for catalyzing the hydration of PO. Nevertheless, most of them still need either high molar ratio of water to PO ($H_2O/PO \geq 10$) or long reaction time for high PG selectivity and yield, and even with low stability. Herein, two homogeneous molecular catalysts were studied for catalytic hydration of PO, and Co^{III}(salen)PF_6 shows better stability than Co^{III}(salen)OTs.

Keywords: Hydration, 1,2-propylene glycol, Molecular catalyst, Stability.

1. Introduction

1,2-propylene glycol (PG) is an important raw material for manufacturing polyester resins, antifreezes, cosmetics, medicines, and other products.[1] Presently, PG is dominantly produced by non-catalytic hydration of propylene oxide (PO) in industry. However, a large excess of water (up to 20 M equiv) is required to obtain high PG selectivity, which makes the production of PG by non-catalytic hydration of PO one of the most cost and energy intense processes in chemical industry.[2] Up to date, various catalysts with acidity or basicity have been developed for PO hydration. Nevertheless, most of them still need either high molar ratio of water to PO ($H_2O/PO \geq 10$) or long reaction time for high PG selectivity and yield. *Li et al.* reported that homogeneous Co^{III}(salen)OTs can catalyze hydration of PO with PG selectivity of ＞99% and PG yield of 96% in 4 h under H_2O/PO of 2.[3] However, Co^{III}(salen)OTs is not stable under reaction condition due to the gradually irreversible transformation into inactive Co^{II}(salen). Herein, a new kind of molecular catalyst, *i.e.* Co^{III}(salen)PF_6, has been discovered to show high stability in catalytic hydration of PO with activity similar to Co^{III}(salen)OTs.

2. Experimental

Co^{III}(salen)PF_6 and Co^{III}(salen)OTs were synthesized according to the reference.[4] For the catalytic reaction, Co^{III}(salen)PF_6 or Co^{III}(salen)OTs, epoxides and H_2O were added into a 10 mL autoclave, then the reaction mixture was stirred at 40 ℃ for desired time interval. After the reaction, the liquid phase was diluted with ethanol and further analyzed by gas chromatography.

3. Results and discussion

Hydration of PO was performed on both Co^{III}(salen)OTs and Co^{III}(salen)PF_6 molecular catalysts under water ratio lower to 2. It has been found that Co^{III}(salen)PF_6 shows similar activity but higher stability in comparison with Co^{III}(salen)OTs, which is also supported by spectroscopic characterization. Figure 1 shows the UV–vis spectra of both Co^{III}(salen)OTs and Co^{III}(salen)PF_6 measured before and after hydration of PO in CH_2Cl_2. It can be learnt that mixing with PO and PG shows almost no influence on the spectrum of fresh Co^{III}(salen)OTs, while the band attributed to inactive Co^{II}(salen) is clearly observed for used Co^{III}(salen)OTs, indicating the transformation of a part of Co^{III}(salen)OTs into Co^{II}(salen) species.

As for Co^{III}(salen)PF_6, the main band at about 360 nm shows an obvious red shift after mixture with PO and PG, which is different from the situation for Co^{III}(salen)OTs. This phenomenon indicates that there is interaction between Co^{III}(salen)PF_6 and PO and/or PG. Notably, the spectrum of used Co^{III}(salen)PF_6 is almost the same as that of the mixture of fresh Co^{III}(salen)PF_6 with PO and PG and no band ascribed to

Co^{II}(salen) is observed for used Co^{III}(salen)PF_6, suggesting the high stability of Co^{III}(salen)PF_6 during hydration process. Therefore, it is confirmed that Co^{III}(salen)PF_6 shows better stability than Co^{III}(salen)OTs.

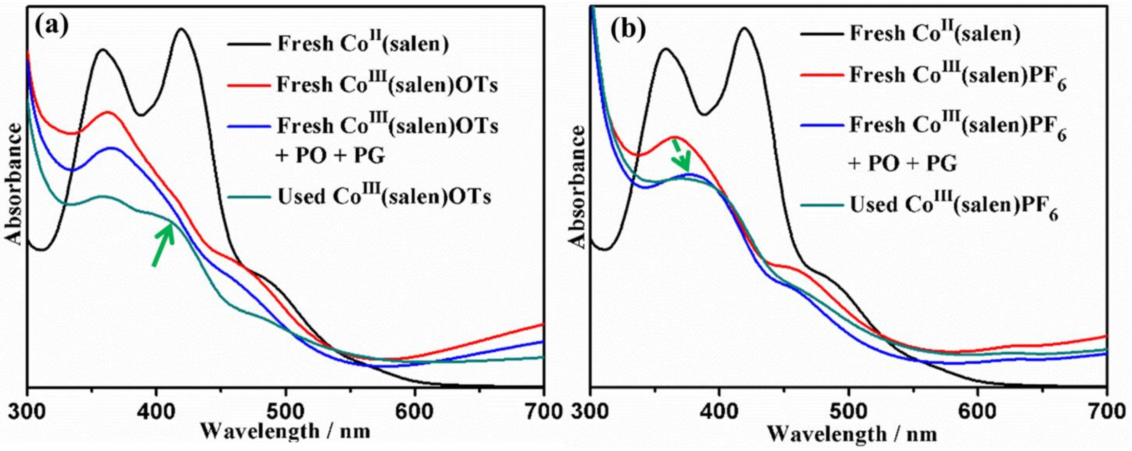

Figure 1. UV–vis spectra of Co^{III}(salen)OTs (a) and Co^{III}(salen)PF_6 (b) measured before and after hydration of PO in CH_2Cl_2.

4. Conclusions

Based on the situations that the non-catalytic method for producing 1,2-propylene glycol (PG) in industry is of high-energy-consumption and the hydration catalyst working under low water ratio is highly desired, two homogeneous Co(salen)-based molecular catalysts were used to catalyze the hydration of PO. Both Co^{III}(salen)OTs and Co^{III}(salen)PF_6 show excellent catalytic activity, while the stability of Co^{III}(salen)PF_6 is better than that of Co^{III}(salen)OTs. These mean that their catalytic behavior may be different and this will be carefully addressed in future.

References

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