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Hydration of Epoxides on [Co^{III}(salen)] Encapsulated in Silica-Based Nanoreactors[**]

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Monoethylene glycol (MEG) and 1,2-propylene glycol (PG) are important raw materials for the manufacture of polyester resins, antifreezes, cosmetics, medicines, and other products.[1] The total global demand for MEG has been estimated to be over 19 million metric tons per year.[2] The production of MEG in industry predominantly involves the liquid-phase hydration of ethylene oxide (EO), whereby a large excess of water (20–25 mol of water/mol of EO) is required for the high conversion of EO and high selectivity for MEG. The concentration of MEG in the final aqueous solution is only approximately 10 wt %, and huge energy is consumed for the distillation of the product from the aqueous solution. As a result, epoxide hydration is one of the most cost- and energy-intensive processes in the chemical industry.

Possible catalytic hydration processes have been extensively investigated for the environmentally friendly production of MEG at a low energy cost. Various types of catalysts, including liquid and solid acids or bases, have been explored, such as sulfuric acid,[3] the salts of some acids,[4] cyclic amines,[5] cation- and anion-exchange resins,[6] quaternary phosphonium halides,[7] polymeric organosilane ammonium salts,[8] macrocyclic chelating compounds,[9] and supported metal oxides.[10] However, a high H_2O/EO molar ratio (i.e. >10) is still required for high MEG selectivity. The MEG selectivity is very low at low H_2O/EO molar ratios owing to the formation of diethylene glycol (DEG) and triethylene glycol (TEG) by the self-condensation of MEG, which is readily catalyzed by acid and base catalysts. Moreover, the inherent corrosion and environmental problems associated with the liquid acids/bases limit their application in industry. The development of an efficient and environmentally benign process for the hydration of epoxides with an H_2O/epoxide molar ratio approaching the stoichiometric value of the chemical reaction is still a huge challenge.

In this study, we developed a solid catalyst that is different from the conventional liquid/solid acid or base catalysts for the hydration of epoxides. We constructed the solid catalyst by encapsulating the molecular catalyst [Co^{III}(salen)], with a salen ligand derived from 3,5-di-*tert*-butylsalicyclaldehyde and *trans*-1,2-diaminocyclohexane,[11] in the nanocage of the mesoporous silica FDU-12. This catalyst exhibits high activity and selectivity in the hydration of epoxides under mild reaction conditions. Furthermore, the H_2O/epoxide molar ratio can be decreased to as low as 2:1 while maintaining the conversion of EO above 98 % and the selectivity for MEG above 98 %. This novel catalytic approach has great potential for the green and energy-saving hydration of epoxides, as well as many other conventional chemical reaction processes in industry.

The solid catalyst (denoted as FDU-12–[Co^{III}(salen)]) was prepared by the encapsulation of [Co^{III}(salen)] molecular catalysts into the nanocages of mesoporous silica (FDU-12); the size of the pore entrance was then reduced by the use of propyltrimethoxysilane as a silylation reagent to prevent the molecular catalysts in the nanoreactor from leaching (for synthesis details, see the Supporting Information).[12] FDU-12 is a mesoporous silica material with a cavity diameter of 18.6 nm and a pore-entrance size less than 4.0 nm.[13] These dimensions make FDU-12 an ideal nanoreactor to host the molecular catalyst (see Figures S1 and S2 in the Supporting Information). According to TEM studies and its N_2-sorption isotherm, FDU-12–[Co^{III}(salen)] also has a cagelike porous structure similar to that of FDU-12, with a uniform distribution of mesopores arranged in cubic *Fm3m* symmetry (Figure 1 A,B). The apparent decrease in the BET surface area and pore volume of the solid catalyst in comparison to FDU-12 is due to the occupation of the nanocages by [Co^{III}(salen)] molecules (see Table S1 in the Supporting Information). FDU-12–[Co^{III}(salen)] has a similar UV/Vis spectrum to that of [Co^{III}(salen)] dissolved in CH_2Cl_2, except for a slight red shift of the UV bands, which suggests a weak host–guest interaction between the nanocages of FDU-12 and [Co^{III}(salen)] (Figure 1 C). NMR spectroscopy confirmed that [Co^{III}(salen)] encapsulated in the nanocages of FDU-12 retains the molecular structure and properties of its free form almost completely (see Figure S3). The molecular catalyst confined in the nanoreactor maintained the behavior of the homogeneous solution of the catalyst. Thus, FDU-12–[Co^{III}(salen)] exhibits the characteristics of both homogeneous and heterogeneous catalysts.

We compared a variety of catalytic processes for epoxide hydration at 40 °C with a 2:1 H_2O/EO molar ratio (Table 1). No product was detected without a catalyst or with only FDU-12 in the absence of the molecular catalyst [Co^{III}(salen)]. The

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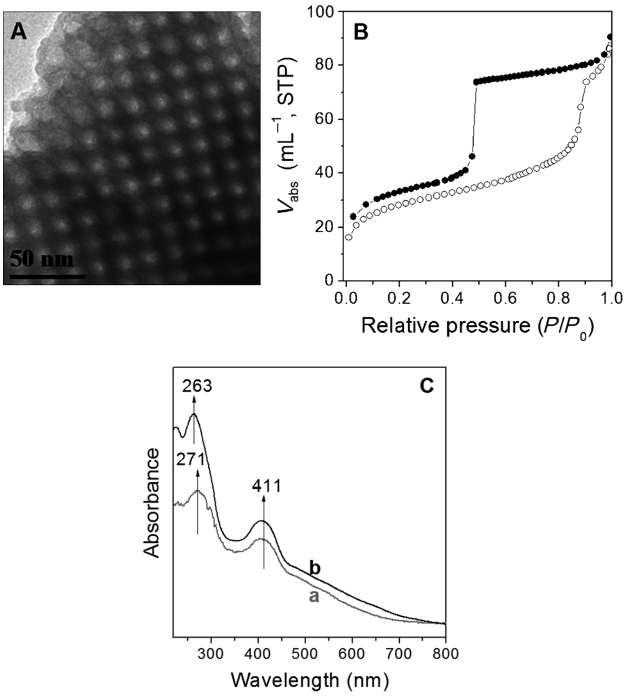


Figure 1. A) TEM image and B) N_2-sorption isotherm of FDU-12–[Co^{III}(salen)]. C) UV/Vis spectra of a) [Co^{III}(salen)] as a solution in CH_2Cl_2 and b) FDU-12–[Co^{III}(salen)]. STP = standard temperature and pressure.

acids $H_3PW_{12}O_{40}$ and H_2SO_4 gave only 66% conversion of EO with 68% selectivity for MEG and 45% conversion of EO with 73% selectivity for MEG, respectively. EO conversion of 8% or less was observed with the ion-exchange resins Amberlite IR 120 and H-ZSM-5 as catalysts. These results show that conventional processes with liquid and solid acid catalysts do not give MEG in high yield when the H_2O/EO molar ratio is close to the stoichiometric value. They are effective only at H_2O/EO molar ratios over 8:1 and high reaction temperatures.[14] FDU-12–[Co^{III}(salen)] can give 98% conversion of EO with selectivity for MEG above 98% (i.e., an MEG yield over 96%). Thus, [Co^{III}(salen)] catalysts confined in the nanocages are very active and selective at a low H_2O/EO molar ratio and mild reaction temperatures.

The catalytic performance of FDU-12–[Co^{III}(salen)] was tested over a wide range of H_2O/epoxide ratios for the hydration of propylene oxide (PO) as a model reaction and compared with that of the conventional liquid acid H_2SO_4 (Figure 2). The use of H_2SO_4 led to less than 80% conversion of PO with H_2O/PO molar ratios between 1:1 and 3:1. When the H_2O/PO molar ratio was increased to 7:1, PO conversion could be increased to 80%. However, the selectivity for the formation of 1,2-propylene glycol (PG) never exceeded 80%, although a slight increase in selectivity was observed when the H_2O/PO ratio was increased. In contrast to H_2SO_4, FDU-12–[Co^{III}(salen)] promoted 92% conversion of PO and showed 98% selectivity for PG even at a 1:1 H_2O/PO molar ratio. Over 98% conversion of PO with more than 98% selectivity for PG were observed with FDU-12–[Co^{III}(salen)] at H_2O/PO molar ratios of 2:1 and above. This result further affirms the high efficiency of the solid catalyst for the hydration of epoxides with a much lower amount of water than is usually necessary.

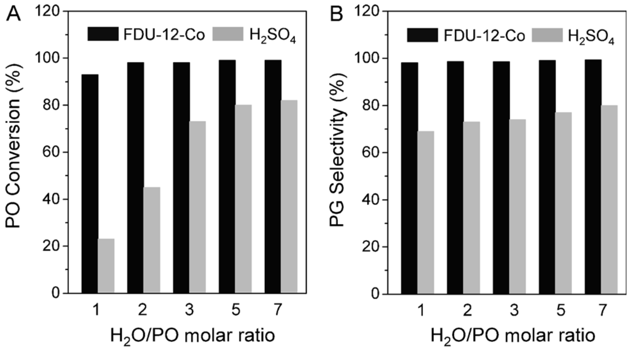


Figure 2. Hydration of propylene oxide (PO) for the production of 1,2-propylene glycol (PG) in the presence of FDU-12–[Co^{III}(salen)] (0.642 wt% Co) and H_2SO_4 at different H_2O/PO molar ratios: A) conversion of PO; B) selectivity for PG. The reactions were performed in PO (50 mmol) with a PO/catalyst molar ratio of 500:1 at 40°C for 3 h.

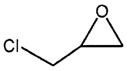
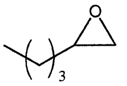
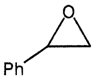
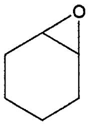
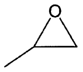
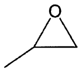
The solid catalyst was also used to catalyze the hydration of a wide range of epoxides at a 2:1 H_2O/epoxide molar ratio for the production of various glycols, which are important intermediates in the fine-chemical and pharmaceutical industries (Table 2). In the hydration of epichlorohydrin, FDU-12–[Co^{III}(salen)] showed 99% conversion of epoxide with 99% selectivity for the glycol. For the more hydrophobic substrates 1,2-epoxyhexane oxide, styrene oxide, and cyclohexane oxide, the catalyst enabled 97, 72, and 46% conversion of the epoxide, respectively, with selectiv-

Table 1: Catalytic hydration of EO for the production of MEG in the presence of conventional catalysts and FDU-12–[Co^{III}(salen)].[a]

Catalyst	*T* [°C]	H_2O/EO [mol/mol]	Conv.[b] [%]	Selectivity[b] [% MEG]	Ref.
–	40	2:1	<1	–	
FDU-12	40	2:1	<1	–	
$H_3PW_{12}O_{40}$	40 (130)	2:1 (8:1)	66 (98)	68 (89)	[14a]
H_2SO_4	40 (50–70)	2:1 (>20:1)	45 (>99)	73 (90)	[14b]
Amberlite IR 120	40 (127–193)	2:1 (20:1)	8 (>99)	72 (70–90)	[14b]
H-ZSM-5	40 (150)	2:1 (22:1)	<1 (98)	– (76)	[14c]
FDU-12–[Co^{III}(salen)][c]	40	2:1	>98	>98	this study

[a] Reactions were performed with H_2O (1.8 mL) and EO (50 mmol) in a 10 mL autoclave under N_2 pressure (1.0 MPa) for 3 h (the pressure was increased to 1.0 MPa by purging with N_2 to keep EO mixed well with H_2O during the catalytic process). The catalyst/EO/H_2O molar ratio was 1:500:1000. The data in parentheses are previous results from studies for which the reference is given in the last column. [b] Conversion and selectivity were calculated on the basis of GC analysis in the presence of octanol as an internal standard. [c] The FDU-12–[Co^{III}(salen)] catalyst contained 0.642 wt% Co.

Table 2: Catalytic performance of FDU-12–[Co^{III}(salen)] and homogeneous [Co^{III}(salen)] for the hydration of various epoxides.[a]

Epoxide	S/C[b]	t [h]	Conv. [%][c]	Selectivity [% glycol][c]
	500	6	> 99 (86)	> 99 (97)
	500	6	97 (69)	> 99 (97)
	250[d]	48	72 (22)	> 99 (> 99)
	250[d]	48	46 (14)	> 99 (> 99)
	500	3	> 98 (87)	> 98 (97)
	2000	12	95 (58)	> 98 (97)

[a] Reactions were performed in epoxide (50 mmol) with a 2:1 H_2O/epoxide molar ratio in the presence of FDU-12–[Co^{III}(salen)] with a Co content of 0.642 wt% at 40 °C. The data in parentheses are for homogeneous [Co^{III}(salen)]. [b] S/C is the molar ratio of the epoxide to [Co^{III}(salen)]. [c] Conversion and selectivity were calculated on the basis of GC analysis in the presence of octanol as an internal standard. [d] THF (1:1 (v/v) with respect to the epoxide) was added.

ity for the glycol above 97%. In comparison with its homogeneous counterpart, the solid catalyst showed much higher conversion of the epoxides and comparable selectivity under identical reaction conditions (Table 2).

Previous studies confirmed that a homogeneous solution of [Co^{III}(salen)] catalyzes the hydration of epoxides through a cooperative activation mechanism; that is, the activity of the reaction can be enhanced when two catalyst molecules cooperate with each other.[11,12b] DFT calculations showed that the activation energies for the bimolecular reaction pathway are significantly lower than that for the monomolecular reaction pathway.[15] This cooperative activation effect is intensified when the molecular catalysts are confined in the nanoreactor, FDU-12. The turnover frequency (TOF) of FDU-12–[Co^{III}(salen)] increases enormously as the number of [Co^{III}(salen)] molecules in each nanocage of FDU-12 increases. This observation suggests that the cooperative activation effect is promoted when the molecular catalysts occupy the narrow space inside the nanoreactor because of the enhanced probability of two molecular catalysts encountering one another (Figure 3 A). The local concentration of [Co^{III}(salen)] in each nanocage (6–18 [Co^{III}(salen)] molecules in an area of 125 nm^3 on average) is much higher than that in the homogeneous catalytic system (1.4 [Co^{III}(salen)] molecules in an area of 125 nm^3 on average; calculated with [catalyst]/[PO]/[H_2O] molar ratio of 1:500:1000) (Figure 3 B). Consequently, the solid catalyst shows much higher activity than the homogeneous catalyst, especially at a high S/C ratio, owing to the enhanced "cooperative activation effect" in the nanoreactor.

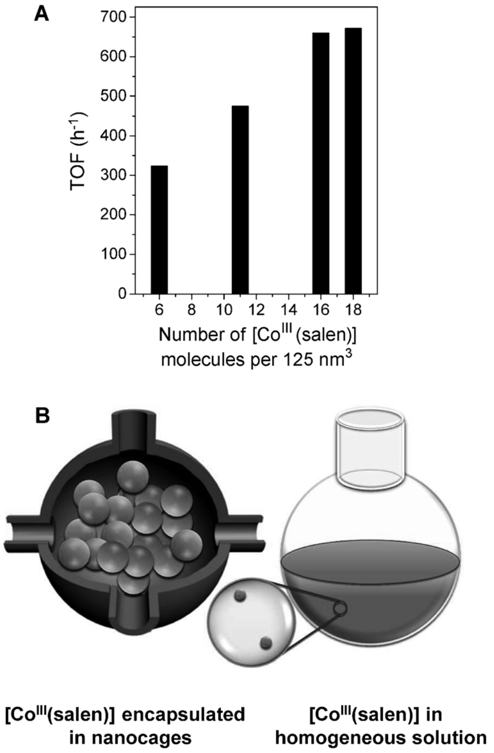


Figure 3. A) TOF of PO hydration in the presence of FDU-12–[Co^{III}-(salen)] with different numbers of [Co^{III}(salen)] molecules in each nanocage. The reactions were performed in PO (50 mmol) with a [catalyst]/[PO]/[H_2O] molar ratio of 1:500:1000 at 40 °C, and the TOFs were calculated for the initial 20 min. B) Illustration of the enhanced cooperative activation effect of [Co^{III}(salen)] for the hydration of epoxides in nanocages (on average 6–18 [Co^{III}(salen)] molecules in nanocages and 1.4 [Co^{III}(salen)] molecules in a homogeneous solution per 125 nm^3).

The observed promotion of the cooperative activation effect between the molecular catalysts in FDU-12–[Co^{III}-(salen)] suggests that [Co^{III}(salen)] catalysts in the nanoreactor can move freely during the catalytic process. The degree of freedom of movement of confined molecular catalysts in the nanoreactor was investigated by ^{31}P NMR spectroscopy. Binapo (2,2′-bis(diphenylphosphinoxy)-1,10-binaphthyl) was chosen as a model catalyst molecule owing to the high natural abundance of ^{31}P and confined in the nanocages of FDU-12 (the sample was denoted as FDU-12–binapo; it was synthesized by a similar procedure to that described for FDU-12–[Co^{III}(salen)] in the Experimental Section). Solid-state ^{31}P NMR spectra of FDU-12–binapo in its solid form and as a suspension in $CHCl_3$ are shown in Figure 4. The static spectrum of the solid sample shows an asymmetric and broad pattern due to the chemical-shift anisotropy of the ^{31}P nucleus (Figure 4 A). The isotropic chemical shift at $\delta = +28$ ppm could be identified by magic-angle spinning at two different speeds (see Figure S4). The static spectra of FDU-12–binapo in the presence of different amounts of solvent are summarized in Figure 4 B. Upon the addition of $CHCl_3$ (10 μL; an amount corresponding to 22%

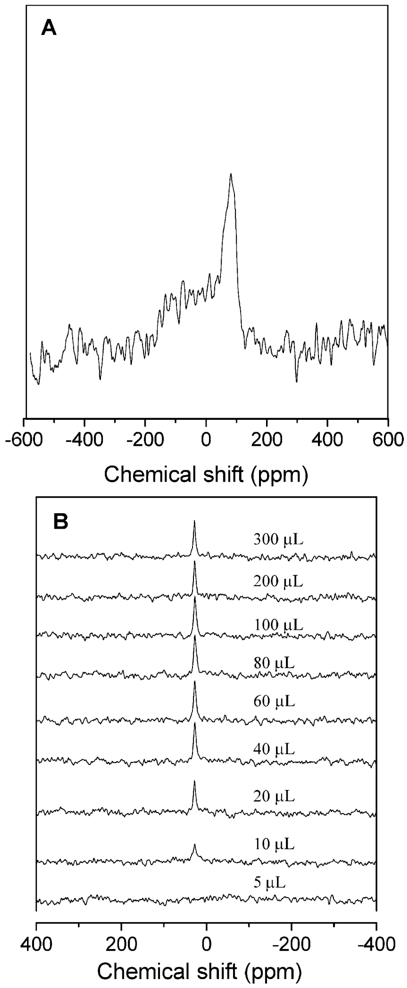


Figure 4. ^{31}P NMR spectra under static conditions of FDU-12–binapo A) in its solid state (NS = 3800 scans) and B) in the presence of different amounts of $CHCl_3$ (as indicated above each spectrum; NS = 128 scans).

of the cage volume filled with $CHCl_3$), a sharp peak appeared at $\delta = +28$ ppm, which indicates that binapo confined in the nanocages of FDU-12 gains some degree of mobility. As the amount of $CHCl_3$ was increased, the peak width of the signal remained almost the same, but the intensity of the signal increased and reached a maximum at a $CHCl_3$ volume of 40 μL (which corresponds to 87 % of the cage volume filled with $CHCl_3$). FDU-12–binapo in the presence of a large enough amount of $CHCl_3$ showed a similar ^{31}P NMR spectrum to that of binapo dissolved in $CHCl_3$ (see Figure S5). These results indicate the fast movement of binapo molecules in the nanoreactor in the presence of a solvent.

Thus, we can deduce that [Co^{III}(salen)] confined in the nanoreactor can move freely during the catalytic process in the presence of reactants and solvent. This proposed behavior is reasonable because there is no strong interaction between [Co^{III}(salen)] and the nanoreactor. The NMR spectroscopic studies clearly show that the catalysis that occurs in the nanoreactor possesses properties of homogeneous catalysis owing to the free movement of the molecular catalysts in the nanoreactor during the catalytic process. Thus, the molecular catalysts encapsulated in the nanoreactor exhibit “homogeneous catalysis in a heterogeneous catalyst”, and the catalytic performance of the solid catalyst, FDU-12–[Co^{III}(salen)], is superior to that of the molecular catalyst, [Co^{III}(salen)], in a homogeneous solution.

This solid catalyst is stable and can be recycled by simple filtration. No leaching of [Co^{III}(salen)] from the solid catalyst was detected during the catalytic process. The slight decrease in activity following the recycling process is possibly due to the incomplete oxidation of [Co^{II}(salen)] to [Co^{III}(salen)] during the catalyst-generation process (see Figures S6 and S7).

A number of approaches have been explored for the immobilization of homogeneous catalysts in attempts to develop greener processes, as immobilized catalysts can be conveniently separated from the reaction system and recycled.[16] However, immobilization through grafting and anchoring of the molecular catalysts on a solid surface (e.g. Al_2O_3 or SiO_2 with a high specific surface area) is often detrimental to their catalytic performance, as the strong interaction with the surface alters the structure and chemical properties of the molecular catalyst. In contrast, the encapsulation of molecular catalysts in a nanoreactor not only maintained their identity but also further improved their catalytic performance as a result of the confinement effect of the nanoreactor. For molecular catalysts that operate by a cooperative mechanism, the number of molecular catalysts accommodated in each cavity can be two or above. However, the number of molecules in each cavity can be precisely limited to one for molecular catalysts that can be deactivated by dimer formation; in this way, deactivation of the catalyst can be avoided effectively.

We have reported a highly efficient solid catalyst, FDU-12–[Co^{III}(salen)], for epoxide hydration at low H_2O/epoxide ratios (1:1–2:1) and low temperature (40 °C). The MEG concentration in the product solution can be increased from 10 wt % (for the noncatalytic hydration process) to more than 75 wt % through EO hydration over FDU-12–[Co^{III}(salen)]. This process is not only energy-efficient but also environmentally benign and therefore holds great potential for industry. We anticipate that this strategy could be extended to the development of many other solid catalysts based on the encapsulation of homogeneous catalysts in solid nanoreactors for the sustainable production of chemicals and pharmaceuticals in industry.

Experimental Section

Typical synthetic procedure for FDU-12–[Co^{III}(salen)]: FDU-12 (1.0 g, dried under vacuum at 125 °C for 6 h) was dispersed in CH_2Cl_2 (5 mL) containing a given amount of [Co^{III}(salen)]. The mixture was stirred at reflux for 12 h under an Ar atmosphere, and then CH_2Cl_2 was removed by evaporation. The resulting solid was added to a mixture of propyltrimethoxysilane (10 mmol) and anhydrous pyridine (1 mL) in dry hexane (2 mL). This reaction mixture was heated at reflux for 12 h under an Ar atmosphere, and the resulting solid was isolated by filtration and thoroughly washed with CH_2Cl_2. The solid product was then dried under vacuum. The Co content of the solid catalysts varied in the range of 0.236–0.725 wt %

on the basis of [Co^{III}(salen)] content in the filtrate and washings after encapsulation by UV/Vis analysis.

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