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Heterogeneous Catalysis

Enhanced Cooperative Activation Effect in the Hydrolytic Kinetic Resolution of Epoxides on [Co(salen)] Catalysts Confined in Nanocages**

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It has been recognized that the cooperative activation by two or more catalytic centers with proper proximity could greatly increase the activity and enantioselectivity of homogeneous chiral catalysts through a specific control of the transition state, like in enzymatic catalysis.[1] If the cooperative activation could be realized in heterogeneous asymmetric catalysis, it may provide new possibilities for the development of high-performance heterogeneous catalysts, especially solid catalysts. This area is of ongoing academic and industrial interest for its potential advantages, such as in the separation and recycling of catalysts, continuous flow operations, and for the easy purification of products.[2]

However, the generation of such a cooperative activation in a solid catalyst is difficult, because of the inability to elaborately control the proper proximity and the relative conformation of the active centers. If transition-metal complexes are confined but allowed to move freely in the isolated nanospace of a porous solid, the proper proximity and the relative conformation of the catalysts required for the cooperative activation could be realized through precisely adjusting the loadings and types of the transition-metal complexes in a confined space. Herein we demonstrate that the cooperative activation effect in the hydrolytic kinetic resolution (HKR) of epoxides could be greatly enhanced by confining [Co(salen)] (salen = (*R*,*R*)-*N*,*N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) complexes in the isolated nanocages of SBA-16 with a high local concentration and thus generated a more active solid catalyst compared with the homogeneous counterpart.

The cagelike mesoporous silica SBA-16 with isolated cages connected by a small pore entrance was chosen as the solid host. In comparison with microporous zeolites, which have pore diameters of less than 2 nm and can also be used as host materials to confine metal complex catalysts,[3] the nanocages of SBA-16 is large enough (the cage size is tunable between 4–ca. 8 nm) to accommodate a desired number of transition-metal complexes in the confined space.[4] The transition-metal complex [Co(salen)] was chosen as the model catalyst because this catalyst has been demonstrated to have a cooperative activation effect in the HKR of terminal epoxides.[5]

After introducing a given number of [Co(salen)] complexes in the nanocages of SBA-16, the pore entrance size was reduced through a silylation reaction. Propyltrimethoxysilane, which has a moderate hydrophobicity, was chosen as the silylating reagent not only to reduce the pore entrance size but also to modify the inner surface of SBA-16, thereby optimizing the diffusion rates of epoxides and H_2O during the reaction. The [Co(salen)] complexes confined in the nanocage of SBA-16 can basically move freely since there are no covalent linkages or other strong interactions between the [Co(salen)] complexes and the surface of SBA-16. We prepared four solid catalysts with different loadings of [Co(salen)] (see the Experimental Section). The solid catalyst, denoted as [Co(salen)]/SBA-16, was characterized by FTIR, UV/Vis, XRD, TEM, and N_2 sorption techniques (see the Supporting Information). Based on an approximate estimation (see the Supporting Information), [Co(salen)]/SBA-16 with a Co content of 0.055, 0.087, 0.157, and 0.225 wt% corresponds to 1.2, 1.9, 3.4, and 4.9 [Co(salen)] complexes, respectively, accommodated in each nanocage of SBA-16.

The catalytic performances of these solid catalysts with different Co contents were evaluated in the HKR of propylene epoxide under identical reaction conditions (Figure 1). The conversion of propylene oxide increases with an increase in the [Co(salen)] loading in the solid catalyst and reaches a plateau at a [Co(salen)] loading above 0.157 wt%. Previous studies have shown that at least two [Co(salen)] complexes are required for cooperative activation.[5] For [Co(salen)]/SBA-16 with 1.2 [Co(salen)] complexes per cage, the reaction is mainly catalyzed by a single [Co(salen)] molecule in the cage of SBA-16. Thus, this catalyst exhibits very low activity (8% conversion with 93% *ee* of the diol). For [Co(salen)]/SBA-16 with 1.9 [Co-

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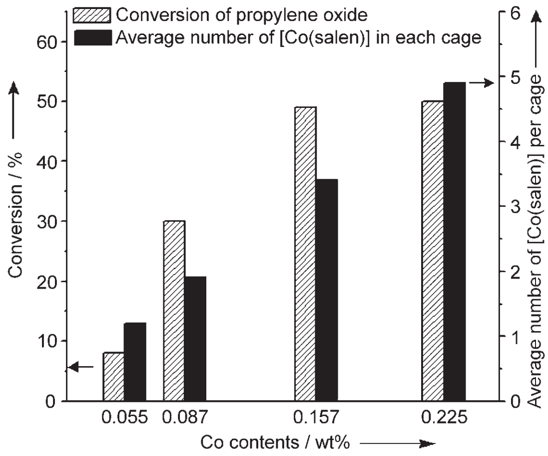


Figure 1. The conversion of propylene oxide on [Co(salen)]/SBA-16 with different loadings of [Co(salen)] complexes per cage. The molar ratio of epoxide to [Co(salen)] was 4000:1; the molar ratio of epoxide to H_2O was 1:0.75; reaction temperature, 283 K; reaction time, 12 h; conversion is calculated according to the following equation: conversion $= (ee_{ep}/ee_{diol})/(1+ee_{ep}/ee_{diol}) \times 100\%$, according to reference [5d].

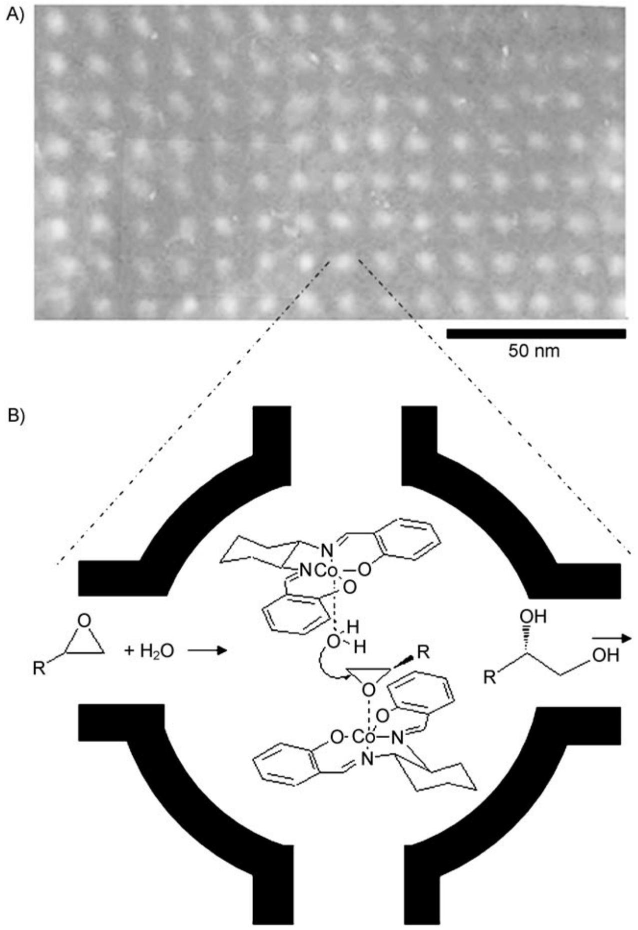


Figure 2. A) TEM image of the (100) projection of cubic SBA-16 (*Im*3*m*); B) schematic representation of the [Co(salen)] catalyst trapped in the isolated nanocage of mesoporous materials, which results in enhanced cooperative activation between reactants on two [Co(salen)] complex molecules for the HKR of epoxides. For clarity, the four *tert*-butyl groups on the 3,5,3′,5′-postions of the salen ligand, the CH_3COO^- group of [Co(salen)], and the propyl groups on the surface of SBA-16 are omitted.

(salen)] molecules per cage, the possibility of the cooperative activation between two [Co(salen)] complexes increases. Consequently, the catalytic activity increases greatly (30% conversion with 94% *ee* of the diol). The [Co(salen)]/SBA-16 catalyst with 3.4 [Co(salen)] complexes per cage exhibits much higher activity (49% conversion with 98% *ee* of the diol) than that with fewer [Co(salen)] complexes per cage. The [Co(salen)]/SBA-16 with 4.9 [Co(salen)] complexes per cage shows a similar catalytic activity as that with 3.4 [Co(salen)] complexes per cage. The [Co(salen)]/SBA-16 catalysts with 1.2, 1.9, 3.4, and 4.9 [Co(salen)] complexes per cage exhibits 93, 94, 98 and 98% *ee* of the diol, respectively (see Table S2 in the Supporting Information). Namely, the enantioselectivity also increases with the increase of the number of [Co(salen)] complexes in each cage.

As a direct consequence of the cooperative activation (or second-order kinetic dependence on the concentration of the catalyst), the overall reaction rate may sharply increase if the local concentration of the catalyst increases. Also, the HKR reaction involves a competition between a highly enantioselective bimetallic pathway (second-order kinetics of the catalysts) and a less enantioselective monometallic pathway.[5b] The increase in the activity and enantioselectivity with an increase in the number of [Co(salen)] complexes per cage primarily indicates that the cooperative activation of [Co(salen)] complexes in the nanocages can be enhanced, as a result of the crowded nature of the cobalt complexes in the nanocages. The appropriate proximity and the free movement of [Co(salen)] in the confined space means that H_2O activated by one [Co(salen)] complex can attack the epoxide activated by another [Co(salen)] complex, and readily produce the diol with high activity (Figure 2). However, too many [Co(salen)] complexes within a confined space may result in a too crowded microenvironment, where mass diffusion becomes a limiting step. This can explain the fact that no further increase in conversion was observed with the [Co(salen)]/SBA-16 catalyst with 4.9 [Co(salen)] complexes per cage (Figure 1).

The catalytic activity of [Co(salen)]/SBA-16 was also compared with that of the homogeneous [Co(salen)] at the same "volume active site density" (the [Co(salen)] density in the whole homogeneous system is kept the same as the local density of [Co(salen)] in the nanocages of SBA-16; see Table S2 in the Supporting Information). It can be clearly seen that the catalytic activity of [Co(salen)] also increases as the density of [Co(salen)] increases, because of the enhanced cooperative activation effect at high [Co(salen)] density in the HKR of terminal epoxides. The catalytic activity of [Co(salen)]/SBA-16 with 1.2 [Co(salen)] complexes per cage is much lower than that of [Co(salen)] when the reaction was performed at the same "volume active site density". This finding can be explained by the fact that it is difficult to induce the cooperation activation effect for the single active site isolated in the nanocages of SBA-16, as mentioned above. In homogeneous catalysis, there is still some possibility for

[Co(salen)] complexes to meet each other even at a low "volume active site density". So the TOF of [Co(salen)] is much higher than that of [Co(salen)]/SBA-16 when the "volume active site density" is low. Upon increasing the volume active site density, the TOF values of the homogeneous catalyst and solid catalyst increased gradually. [Co(salen)]/SBA-16 with more than 1.9 [Co(salen)] complexes per cage exhibits only slightly lower TOF values than [Co(salen)] because of the mass diffusion limitation for the heterogeneous system. This result also strongly supports the formation of the cooperative activation effect in [Co(salen)]/SBA-16 with a high [Co(salen)] density.

To further understand the enhanced cooperative activation effect in the nanocage, we compared the catalytic performances of the homogeneous [Co(salen)] and [Co(salen)]/SBA-16 (with a Co content of 0.157 wt %) for the HKR of propylene epoxide at high substrate/catalyst (S/C) ratio (the molar ratio of racemic epoxide to [Co(salen)]; Table 1). Homogeneous [Co(salen)] affords 34 % conversion at a S/C of 4000:1. Under the similar conditions, [Co(salen)]/SBA-16 gives 49 % conversion. The catalytic activity of [Co(salen)]/SBA-16 is higher than that of the homogeneous catalyst (TOF: 163 h^{-1} versus 113 h^{-1}). When the S/C ratio increases from 4000:1 to 12 000:1, the conversion for the homogeneous catalyst sharply decreases from 34 % to 7 % even though the reaction time is prolonged to 24 h, and the TOF decreases from 113 h^{-1} to 35 h^{-1}. The enantioselectivity simultaneously decreases from 98 % *ee* to 89 % *ee*. In contrast, under similar conditions, [Co(salen)]/SBA-16 can still afford 50 % conversion with 98 % *ee* of the diol at a S/C ratio of 12 000:1 (the average TOF increases because the reaction undergoes an induction period for the solid catalyst, see the kinetic plots in the Supporting Information). Thus, [Co(salen)] confined in the nanocage displays much higher activity and enantioselectivity in the HKR of propylene epoxide than the homogeneous counterpart, especially at high S/C ratios.

Table 1: Hydrolytic kinetic resolution of racemic propylene oxide on homogeneous Co(salen) catalyst and heterogeneous [Co(salen)]/SBA-16 catalyst.[a]

Catalysts	S/C[b]	Conv[c] [%]	*ee* of ep[d] [%]	Diol[e] *ee* [%]	TOF[f] [h^{-1}]
[Co(salen)]	4000:1	34	52	98	113
[Co(salen)]/SBA-16	4000:1	49	96	98	163
[Co(salen)]	12 000:1	7	7	89	35
[Co(salen)]/SBA-16	12 000:1	50	98	98	250

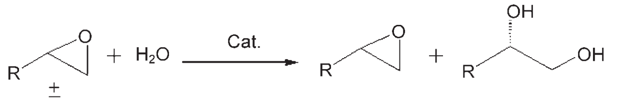
[a] The Co content in [Co(salen)]/SBA-16 is 0.157 wt % (3.4 [Co(salen)] complexes in each cage) based on the ICP analysis; the molar ratio of epoxide/H_2O is 1:0.75; reaction temperature, 283 K; reaction time at S/C of 4000:1 and 12000:1 was 12 and 24 h, respectively. [b] The molar ratio of racemic epoxide to [Co(salen)]. [c] Conversion is calculated according to the following equation: conversion $= (ee_{\mathrm{ep}}/ee_{\mathrm{diol})/}(1+ee_{\mathrm{ep}}/ee_{\mathrm{diol})} \times 100\,\%$, according to reference [5d]. [d] The *ee* value of epoxides was determined by GC with a chiral stationary phase (see the Supporting Information). [e] The *ee* value of the diol was determined by GC with a chiral stationary phase. [f] TOF (average) is calculated according to the following equation: $\mathrm{TOF} = N_{\text{conversed propylene oxide}}/(N_{[\mathrm{Co(salen)}]} \times t)$, where N denotes molar numbers, and t denotes reaction time (h).

The concentration of [Co(salen)] in the reaction system greatly affects the conversion and enantioselectivity in the HKR of epoxides because at least two [Co(salen)] complexes are needed to generate the cooperative activation.[5b] For homogeneous HKR of epoxide, at S/C ratios of 4000:1 and 12 000:1, it is estimated that there are 3.4 [Co(salen)] complexes in a volume of 1580 and 4740 nm^3, respectively. This means that the "volume active site density" decreases to 1/3 when the S/C ratio increases from 4000:1 to 12 000:1. Clearly, the possibility for [Co(salen)] complexes to meet each other decreases at higher S/C ratios, therefore reducing the possibility for cooperative activation. Thus, the catalytic activity drops greatly as the S/C ratio increases (Table 1). To generate an efficient reaction system at high S/C ratios for the HKR of epoxide, the [Co(salen)] complexes should be spatially close enough to enhance the cooperative activation as previously demonstrated by the research group of Jacobsen and others.[5a,b,6] The [Co(salen)]/SBA-16 with Co content of 0.157 wt % has 3.4 [Co(salen)] complexes in each nanocage, which corresponds to 3.4 [Co(salen)] complexes in a volume of 65 nm^3. Therefore, the local density of [Co(salen)] in the nanocage is much higher than that of the homogeneous system. Consequently, [Co(salen)]/SBA-16 with a Co content of 0.157 wt % exhibits much higher catalytic activity than its homogeneous counterpart, even at high S/C ratios. Since the local density of [Co(salen)] in each cage remains the same regardless of the change in the S/C ratio, the catalytic activity does not apparently decrease when the S/C ratio increases. The higher catalytic activity and enantioselectivity of [Co(salen)]/SBA-16 than the homogeneous counterpart at high S/C ratio is clearly a consequence of the reinforced cooperative activation effect arising from the high local density of [Co(salen)] complexes in the nanocage. This is the reason why [Co(salen)]/SBA-16 shows higher TOF values than the homogeneous system (Table 1), despite the mass-diffusion limit for the heterogeneous system.

Such enhanced activity of [Co(salen)]/SBA-16 was also observed in the HKR of other types of epoxides at high S/C ratios (Table 2). For styrene oxide, [Co(salen)]/SBA-16 gives 22 % conversion with 84 % *ee* of the diol at an S/C ratio of 2000:1; however, homogeneous [Co(salen)] exhibits nearly no activity. The similar tendency was also observed in the HKR of phenyl glycidyl ether. [Co(salen)]/SBA-16 gives 52 % conversion with 86 % *ee* of the diol at an S/C ratio of 10 000:1; whereas homogeneous [Co(salen)] affords only 9 % conversion with 84 % *ee* of the diol under the same conditions.

To evaluate the stability of the solid catalysts we investigated recycled [Co(salen)]/SBA-16 with a Co content of 0.157 wt % (3.4 [Co(salen)] complexes per cage) in the HKR of propylene oxide (Table 3). The solid catalyst can be easily recovered by centrifugation or filtration and regenerated by treatment with dilute acetic acid in air. A 43 % yield of the diol with 98 % enantioselectivity was obtained even after eight consecutive cycles of the reaction. No apparent loss of activity and enantioselectivity was observed for the reused catalyst. The Co content in the filtrate of the reaction was below the detection limits of ICP-AES analysis. This further

Table 2: Hydrolytic kinetic resolution of different terminal epoxides with homogeneous [Co(salen)] and heterogeneous [Co(salen)]/SBA-16 catalysts.[a]



R	S/C[b]	*T* [k]	Conv[e] [%]	*ee* of ep [%]	*ee* of diol [%]
Ph	2000:1 (homo.)[c]	303	2[f]	2	2
Ph	2000:1 (hetero.)[d]	303	22	23	84
$PhOCH_2$	10000:1 (homo.)	298	9	8	84
$PhOCH_2$	10000:1 (hetero.)	298	52	93	86

[a] The molar ratio of epoxide to H_2O is 1:0.75; reaction time, 48 h. [b] The molar ratio of racemic epoxide to [Co(salen)]. [c] Homo. refers to homogeneous [Co(salen)]. [d] Hetero. refers to solid catalyst [Co(salen)]/SBA-16. [e] The conversion is calculated according to the equation in footnote [c] of Table 1. [f] The conversion is estimated based on the *ee* value of epoxides.

Table 3: Recycling test of [Co(salen)]/SBA-16 with a Co content of 0.157 wt% (3.4 [Co(salen)] complexes in each cage) in the HKR of propylene oxide.[a]

Cycle times	Reaction time [h]	Diol yield [%][b]	Diol *ee* [%]
1	12	43	98
2	12.5	44	97
3	12.5	45	98
4	12.5	46	98
5	13	46	98
6	14	45	97
7	15	46	97
8	18	43	98

[a] The molar ratio of epoxide/H_2O 1:0.75; S/C 4000:1; reaction temperature 283 K. [b] GC analysis using nonane as an internal standard.

indicates that the HKR reaction takes place in the nanocages of SBA-16 and there was no evident leaching of the [Co(salen)] from the solid catalyst.

In conclusion, we have demonstrated for the first time that the cooperative activation effect can be enhanced in the nanocage of mesoporous materials. By accommodating the [Co(salen)] complexes in the nanocages of SBA-16, an efficient solid chiral catalyst for the hydrolytic kinetic resolution of epoxides has been developed. The solid catalyst exhibits significantly higher activity and enantioselectivity than the homogeneous [Co(salen)] in the HKR of epoxides at high S/C ratios. The solid catalyst can be easily recycled by filtration without any apparent loss of catalytic activity and enantioselectivity. The nanocages of mesoporous materials can be used as nanoreactors to confine metal complexes with a high local concentration and thus lead to the crowded microenvironment of the complexes that enhance the cooperative activation. This work provides a new opportunity for the design of efficient solid catalysts for the asymmetric reactions as well as many other reactions, which involve cooperative activation by separate catalytic centers or second-order kinetic dependence on the local concentration of catalysts.

Experimental Section

SBA-16 (0.5 g, evacuated at 398 K for 6 h) was dispersed in dichloromethane (3 mL) containing the desired amounts of [Co(salen)] (0.0040, 0.0125, 0.0500, and 0.0800 g). After stirring the mixture at 313 K for 24 h under Ar, the CH_2Cl_2 was removed by evaporation. The resultant solid was introduced to a solution containing dried toluene (0.62 g), anhydrous pyridine (0.70 g), and propyltrimethoxysilane (0.70 g). After refluxing the mixture for 24 h under Ar, the resultant solid was isolated by filtration, washed thoroughly with THF, and dried in vacuum. The resultant solid catalyst was denoted as [Co(salen)]/SBA-16.

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