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Tailoring the Window Sizes to Control the Local Concentration and Activity of (salen)Co Catalysts in Plugged Nanochannels of SBA-15 Materials**

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Organometallic complexes with excellent activity and selectivity have found many applications in homogeneous catalysis for the transformation of organic molecules. The use of chiral metal complexes in particular has facilitated the economically viable synthesis of enantiopure organic compounds with a global market of 5.3 billion US$ in 2011 with an annual growth rate of 6.5%.[1] Among these, chiral (salen)metal complexes catalyze many asymmetric transformations of, for example, the hydrolysis of terminal epoxides through hydrolytic kinetic resolution (HKR) into single enantiomers.[2–5] The reaction kinetics are second order in catalyst concentration through the close proximity of two metal complexes in the activation of the substrates, which resembles the active site of an enzyme (Supporting Information, Scheme S1).[6–9]

Increased local concentration of these metal complexes by confinement would be highly desirable to enhance their performance. The "ship-in-a-bottle synthesis" of metal compounds in the micropore structure of zeolites by diffusing small precursors and building up complexes larger than the window sizes of the pore turned out to be a promising approach to immobilize these complexes.[10–13] The resulting catalysts display the beneficial properties of homogeneous catalysts, namely high selectivity and activity, and of heterogeneous catalysts through facile recovery and reuse. However, the small pore sizes (less than 1 nm) of zeolites limit the scope of applications of ship-in-a-bottle catalysts.

Silica-based nanoporous (2–20 nm) materials, synthesized using supramolecular templates, are better alternatives for catalysis because of their larger pore sizes and various pore geometries.[14–16] Among others, SBA-16 and FDU-12 with (3D) cage-like pore structures in which each cage is interconnected to 8 or 12 neighboring pores, respectively, by smaller windows have been used to encapsulate either pre-synthesized (salen)Co complexes followed by silylation[17,18] or pre-synthesized ligands.[19] The catalysts obtained using the former approach were superior to the homogeneous catalyst in terms of activity and selectivity,[17] while those obtained through the latter approach showed lower activity compared to the homogeneous catalyst.[19] A main challenge of host–guest catalysis is the decrease in activity owing to the limits of mass transfer relating to the small window sizes (Figure 1). Therefore, tailoring the window sizes might enhance the performance of catalysts confined within nanoporous supports.

Inspired by these results we searched for new nanoporous supports and related the performance of confined metal complexes with the nanocavity accessibility. Open-ended (1D) nanochannel materials, for example SBA-15, have been used widely in immobilization, but their application to ship-

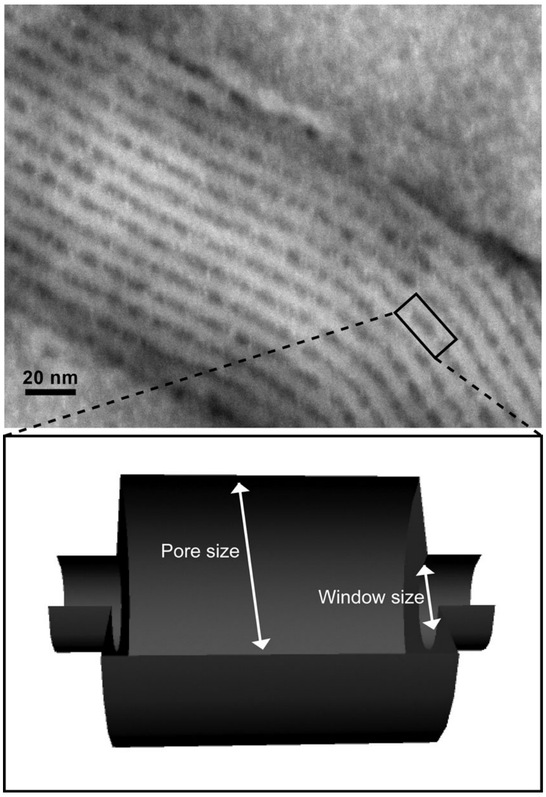

Figure 1. The high-angle annular dark-field (HAADF) image of the plugged nanochannels of SBA-15 after Pt staining (top). Scheme of a plugged nanochannel in which pore and window sizes are controlled by the time and temperature of the synthesis (bottom).

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in-a-bottle synthesis is still not possible. Van der Voort and co-workers, reported the synthesis of a new type of SBA-15, so-called plugged SBA-15, that combines the features of conventional SBA-15 and short nanochannels aligned through two smaller windows[20,21] and synthesis of these materials was later modified by other research groups.[22,23] The plug formation in SBA-15 materials has been studied by X-ray diffraction and gas physisorption. The plugged SBA-15 materials possess low pore volume, but enhanced wall thickness and thermal and mechanical stability compared to conventional SBA-15. We recently reported a reproducible procedure for the synthesis of plugged SBA-15 materials which enables manipulation of the window (2–5 nm) and pore (4–7 nm) sizes with sub-nanometer precision by carefully varying the time and/or temperature of the synthesis.[24]

Herein, we report TEM studies and assess the suitability of (1D) plugged nanochannels of various SBA-15 materials with well-defined window sizes to host (*S*,*S*)-(+)-*N*,*N*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt(III) (chiral (salen)Co^{III}) complexes through ship-in-a-bottle synthesis from external precursors for the first time. The chiral (salen)Co^{III} complex in plugged nanochannels of SBA-15 materials were used in the HKR of terminal epoxides. We were able to control the (local) catalyst concentration and activity of the confined metal complexes in plugged nanochannels of SBA-15 materials by changing the size of the window. The results showed that the ship-in-a-bottle synthesis from external precursors with control over the window sizes was a key factor for maximal activity of the confined metal complexes in the host materials.

Plugged SBA-15 materials with tailored pore and window sizes and a sample of conventional SBA-15 were synthesized by changing the time and/or temperature of the hydrothermal treatment.[24,25] The structural properties of (plugged) SBA-15 materials obtained from N$_2$ isotherms (Figure S1) are given in Table S1. The (plugged) SBA-15 materials after staining with Pt were characterized by transmission electron microscopy (TEM; Figure 1; Figure S3). The results for the first time clearly show that plugged SBA-15 consists of aligned short nanochannels (the length is a few times the diameter) connected through smaller windows making them suitable for the ship-in-a-bottle synthesis of metal complexes, while conventional SBA-15 consists of long open nanochannels. The inner surfaces of (plugged) SBA-15 materials were modified by *n*-propyltrimethoxysilane to cap the silanol groups and adjust the size of the windows (Figures S4–S8 and Table S2).[24] The structural properties of the modified (plugged) SBA-15 including the calculated window sizes are given in Table 1. The chiral (salen)Co^{III} complexes were built up using the ship-in-a-bottle synthesis inside the modified (plugged) nanochannels of SBA-15 from the external precursors under mild reaction conditions, which was followed by thorough washing to remove physically adsorbed complexes (Scheme S2).[11,12] Chiral (salen)Co^{III} catalysts in four different plugged nanochannels of SBA-15 are designated as catalysts **1**–**4** and that in conventional SBA-15 as catalyst **5** (Table 1).

Table 1: Characteristics of chiral (salen)Co^{III} in (plugged) nanochannels of SBA-15 materials.

Host material	Catalyst	Pore size [nm]	Window size [nm]	Loading [mg g^{-1}][a]	*N*[b]
plugged SBA-15	**1**	4.0	1.0	16.0	5.9
	2	4.4	1.6	18.0	5.8
	3	4.2	1.8	15.0	4.8
	4	4.6	2.2	9.0	2.7
SBA-15	**5**	6.3	6.3	0.0	0

[a] Loading indicates the amount of chiral (salen)Co^{III} in mg per gram of modified (plugged) SBA-15 material. [b] *N* is defined as the number of chiral (salen)Co^{III} complexes per 100 nm^3 of modified (plugged) SBA-15 pore volume.

The formation of chiral (salen)Co^{III} inside the modified plugged SBA-15 materials was investigated by FTIR spectroscopy, UV/Vis spectroscopy, elemental analysis, and N$_2$ physisorption. The FTIR spectrum of catalyst **4** showed a strong and characteristic C=N vibration at 1624 cm^{-1}, indicating the presence of the salen ligands in the plugged nanochannels of SBA-15 (Figure S9).[4] UV/Vis spectra of catalysts **3** and **4** suggested the formation of the (salen)Co complex because of the absence of a peak at 334 nm (n-π^*) and the presence of a strong peak at 410 nm (d-π^*) corresponding to cobalt complexation with salen ligands (Figure S10). The N$_2$ physisorption of catalysts **1**–**5** showed that (plugged) SBA-15 materials maintained their original features (Figure S4–S8) and were accessible enough to facilitate mass transfer during catalysis. These results indicated the presence of an intact chiral (salen)Co^{III} complex inside plugged nanochannels of SBA-15 materials.

Tailoring the window sizes influences the (local) concentration of the metal complexes in the nanocavities by controlling their diffusion during synthesis and their retaining power during washing steps. Loadings of 16.0, 18.0, 15.0, and 9.0 mg of the chiral (salen)Co^{III} per gram of support in catalyst **1**–**4** were obtained from the elemental analysis (Table 1), respectively. For catalysts **2**–**5**, the trend shows that a smaller window size increases the ability of the cavity to retain the complex during washing. The low loading of complex with catalyst **1** might be caused by limitations of diffusion during the synthesis, as the window size is only 1.0 nm. The local concentration of the active sites (*N*; number of chiral (salen)Co^{III} complexes per 100 nm^3) were 5.9, 5.8, 4.8, and 2.7 for the window sizes of 1.0, 1.6, 1.8, and 2.2 nm, respectively (Table 1). This indicates an average number of ten chiral (salen)Co^{III} molecules per nanocavity for catalyst **3**.

The obtained catalysts were used in the HKR of 1,2-epoxyhexane and all of them were active without the need of pre-activation. In contrast, the catalyst synthesized through encapsulation of (salen)Co complexes by Li and co-workers initially was inactive and was reactivated by the HKR of a batch of propylene oxide.[17] Catalysts **1**–**4** showed much higher activity than the homogeneous catalyst for the same catalyst loading (0.015 mol.%) suggesting the synergy of bimetallic cooperation inside the plugged nanochannels by increasing the local concentration of the active sites from 0.8 to 2.7–5.9 (Table S3; entries 1–4 versus entry 6).

The activity of the catalysts changed significantly by varying the window sizes and *N* (Figure 2). The activity

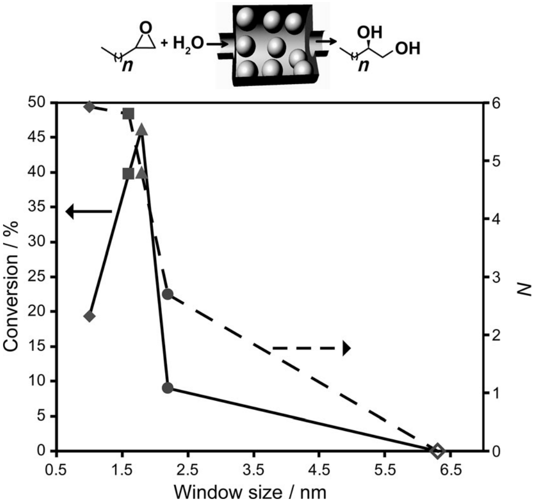

Figure 2. Percent conversion of 1,2-epoxyhexane and *N* (number of chiral (salen)Co^{III} complexes per 100 nm^3) versus window size by catalyst **1** (◆), **2** (■), **3** (▲), **4** (●), or **5** (◇). Reactions conditions: catalyst loading of 0.015 mol% (percent molar ratio of confined chiral (salen)Co^{III} relative to 1,2-epoxyhexane), 0.75 equiv H_2O (relative to 1,2-epoxyhexane), room temperature, and reaction time of 48 h. The scheme shows the HKR of terminal epoxides using a confined chiral (salen)Co^{III} (spheres) inside the plugged nanochannel of SBA-15. The maximum theoretical conversion is 50%. For further details see Supporting Information, Table S3.

initially increased with increased window sizes and reached a maximum at 1.8 nm when *N* was still high enough and then decreased sharply with further increases in the size of the window because of the much lower *N* that was achieved (Figure 2; Table S3). Catalyst **2** with a larger window size than catalyst **1** (1.6 nm versus 1.0 nm), despite a similar *N* value, showed a twofold increase in conversion while both provided high enantioselectivity (> 99%). Catalyst **3** (only 0.2 nm larger window size than **2**) had a lower *N* but showed higher activity, possibly arising from faster mass transfer. Catalyst **4** with a still larger window size (2.2 nm) but *N* being half that of catalysts **2** and **3**, gave about fourfold lower conversion, confirming that the reaction rate follows a second-order dependency on the local concentration of catalyst.[6] Catalyst **5** showed no conversion owing to a low loading of chiral (salen)Co^{III} complexes. Consequently, the activity of the catalysts showed a strong dependence on the size of the window and increased with the window size, provided that the bimetallic cooperation effect is satisfied by $N \geq 5$.

We then compared the turnover frequency (TOF) of chiral (salen)Co^{III} in plugged SBA-15 and that in SBA-16, relative to the homogeneous catalyst in the corresponding study.[17–19] The TOF of chiral (salen)Co^{III} in SBA-16 obtained through encapsulation of metal complexes was sevenfold higher than the homogeneous counterpart (Table S4, entry 1).[17] However, the TOF of catalyst **3** in this study was 35-fold higher than the homogeneous counterpart (Table S4, entry 2). Clearly, the ship-in-a-bottle synthesis from external precursors with tailoring of the window sizes used here is a more efficient strategy for achieving high activity of the confined metal complexes.

HKR with more aliphatic terminal epoxides with longer and shorter alkyl chains under the same reaction conditions and recyclability of the catalysts were conducted. The size of the substrate and hydrophobic interaction of the substrate with its host influence diffusion inside the cavity and consequently the reaction rate.[26] Catalyst **3** resolved the terminal epoxide of 1,2-epoxydecane with a very long alkyl chain and higher viscosity in the absence of any solvent at similar reaction rates for 1,2-epoxyhexane and higher than that of 1,2-epoxypropane (Table S5). Catalyst **3** could be recycled at least four times, operating for a total of 200 hours while maintaining its activity and enantioselectivity (Figure S11). The isolated reaction mixture from the first batch was supplied with a new batch of substrate and the conversion was followed over time. No additional conversion was observed after 48 hours, which together with the stable performance of the catalyst over the runs confirms the absence of leaching. Consequently, these results showed that the obtained catalysts meet the criteria of a stable heterogeneous catalyst, while accepting various substrates.

We presented for the first time the use of one-dimensional plugged nanochannels of SBA-15 materials to host metal complexes using ship-in-a-bottle synthesis. The metal complex loading in the plugged nanochannels of SBA-15 depends on the window size which controls the synthesis and protects against washing. The activity is strongly affected by the size of the window, increasing with the window size provided that bimetallic cooperation is still effective. The ship-in-a-bottle synthesis of chiral (salen)Co^{III} complexes from external precursors with tailored window sizes resulted in a large enhancement of activity compared to the homogeneous catalyst. Our finding for plugged SBA-15 materials, that a simple change of hydrothermal treatment conditions allows tailoring of the window sizes for the nanocavities for maximum performance of the confined catalysts, might be applicable in other fields of host–guest chemistry.

Experimental Section

The synthesis of chiral (salen)Co^{III} complexes in plugged nanochannels of SBA-15 materials was conducted using ship-in-a-bottle synthesis. The inner surfaces of (plugged) SBA-15 materials were first modified with *n*-propyltrimethoxysilane to cap the silanol groups and vary the size of the windows. The ship-in-a-bottle synthesis inside the modified (plugged) SBA-15 materials was conducted by diffusing the precursors one-by-one under mild reaction conditions, oxidating the chiral (salen)Co^{II} by acetic acid in toluene (1:9) under air, and washing the catalysts thoroughly with toluene, methanol, and dichloromethane then drying under vacuum. Catalysts **1**–**5** (see Table 1) then were used in the hydrolytic kinetic resolution of the terminal epoxides.

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