

Highly active new chiral Co(III) salen catalysts immobilized by electrostatic interaction with sulfonic acid linkages on ordered mesoporous SBA-16 silica

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New chiral cobalt(III) salen complexes immobilized via HO₃S-linkers on ordered SBA-16 by electrostatic interactions showed very high activity in enantioselective ring-opening reactions of racemic epoxides.

Here, the new application of sulfonic acid (–SO₃H) functionalized SBA-16 is introduced as an effective method for the immobilization of chiral salen complexes on surfaces. This approach is so simple that it can provide a facile route for anchoring the active sites in one step as compared to covalent attachment which requires complicated procedures in the synthesis of various functionalized linkers.^{1,2} Aromatic SO₃^(–) anion containing homogeneous chiral Co(III) salen complexes have been successfully prepared and used as active catalysts by the Jacobson group.^{3,4} Those homogeneous cobalt(III)-salen complexes bearing a sulfonic acid group (as a charge-balancing anion) exhibited high activity and enantioselectivity in asymmetric ring opening (ARO) reactions of racemic epoxides by various nucleophiles. However, the immobilization of cobalt(III) salen complexes by electrostatic interactions with alkyl and aromatic sulfonic groups *via* HO₃S-functionalized linkers on inorganic supports, and the application of those heterogenized complexes in chiral catalysis have not been reported. Our main methodology is the direct oxidation of monomeric cobalt(II) salen by an SO₃H group linked through propyl- or phenethyl-silane *via* ionic pair formation^{5,6} on the support to yield catalytically active chiral cobalt(III)-SO₃ salen species. In this context, mesoporous materials containing sulfonic acid groups were chosen as candidates for immobilization of cationic chiral salen complexes. During the reaction between monomeric cobalt(II) salen and HO₃S-functionalized SBA-16 under air bubbling in toluene, the cobalt(II) salen became oxidized to cobalt(III), and the increased +1 charge of cobalt(III) in salen would be balanced by the SO₃^(–) anion linked to the tether on support surfaces, providing a strong and stable linkage as ionic pairs. Unreacted cobalt(II) salen ligand remained in the +2 oxidation state in solution without attachment.

Furthermore, for the purpose of anchoring chiral salen complexes to the inorganic supports, we investigated the synthetic method how to obtain sulfonic acid-functionalized SBA-16 materials by direct co-condensation of alkoxysilane

and organosilane compounds in the presence of surfactants and H₂O₂. Alternatively, the addition of mercaptopropyl-triethoxysilane (MPTES) or 2-(4-chlorosulfonylphenyl)ethyl-trimethoxysilane (CSPTMS) into the reactant mixtures for SBA-16 was adopted for introducing sulfonic acid groups on their pore walls. The active sulfonic group was formed through the oxidation of propanethiol or chlorosulfonylphenyl groups during the synthesis of mesoporous SBA-16 materials by H₂O₂.

The MTPES (or CSPTMS) functionalized SBA-16 materials were prepared using EO₁₀₆PO₇₀EO₁₀₆ (F127; Aldrich) as a structure directing agent. The molar composition of each substrate for 1 g of copolymer (as a basis) was X TEOS: (0.0227 – X) MPTS or CSPTMS precursor : 0.0405 BuOH : 0.0201 HCl : 2.74 H₂O : Z H₂O₂; where X = 0.0227 (0%), 0.0204 (10%), 0.0183 (20%) or 0.0159 (30%). The numbers in parentheses indicate the percentage of silicon as MTPES (from Aldrich) (or CSPTMS (from Gelest) in the initial mixture. Some approaches have been demonstrated in the synthesis of the sulfonic acid-functionalized SBA-15 or MCM-41 materials by direct one-pot condensation reaction between TEOS and organosilane compounds CSPTMS (or MPTES) in the presence of surfactants and H₂O₂.^{7–10} To the best of our knowledge, the synthesis of sulfonic acid-containing SBA-16 material has not been explored to date.

In direct incorporation of sulfonic group on the surfaces, too large a content of MPTES or CSPTMS in the starting synthetic mixtures lowers the regularity of the mesopores, and thus there is a limitation on the concentration of acid sites on the mesoporous materials. Table 1 summarizes the preparation conditions and the physicochemical properties of the sulfonic-modified SBA-16 materials. The BET surface areas and pore volumes were decreased as the introduced amount of MTPES or CSPTMS increased.

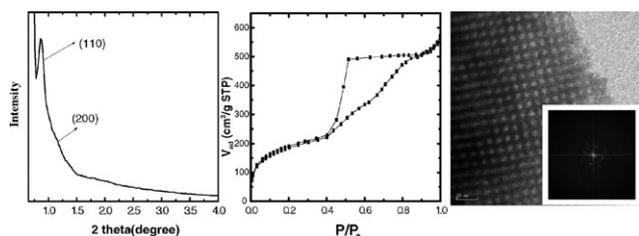
For the SBA-16 samples synthesized with CSPTMS/ (CSPTMS + TEOS) molar ratio of 0.2, the XRD result (in Fig. 1) confirmed that the CSPTMS-functionalized SBA-16 material possess a cubic ordering, as evidenced by the appearance of the (110), (200) peaks with additional broad peaks at 2θ = 2.0°. N₂ adsorption/desorption isotherms of sulfonic acid-functionalized SBA-16 are the type IV (H₂) hysteresis loop that is typical for mesoporous materials with ordered cubic channels. The TEM image shown in Fig. 1 also confirms the high mesoscopic order of arenesulfonic functionalized mesoporous silicas synthesized in this work, showing that SBA-16 has a regular cubic array of uniform channels.

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Table 1 Physicochemical and textural properties of extracted SBA-16 samples containing sulfonic acid moieties

No	Organosilane	Molar composition		Textural properties			Sulfur content ^b	Incorporation (%)
		X	Z	Pore size ^a /Å	S _{BET} /m ² g ⁻¹	V _p /cm ³ g ⁻¹		
1	MTPES	0.0204	0.0204	38	885	1.41	1.39	83 ^c
2	MTPES	0.0183	0.0183	46	664	0.82	2.50	75 ^d
3	CSPTMS	0.0204	0.0102	32	826	1.23	1.34	80 ^c
4	CSPTMS	0.0183	0.0102	43	780	0.96	2.37	71 ^d

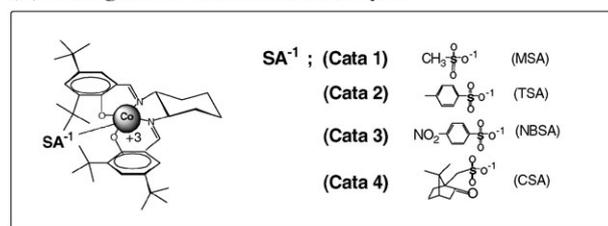
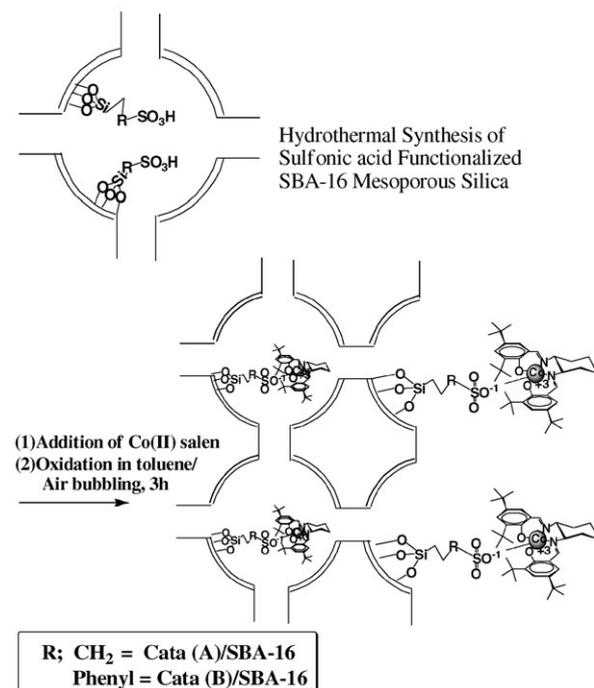
^a Mean pore size from adsorption branch applying the BJH model, ^b mmol of sulfur per g-SiO₂, ^c 1.67 mmol and ^d 3.34 mmol of sulfur per g-SiO₂ (as a theoretical value).

**Fig. 1** XRD pattern, N₂ isotherm and TEM image of the [110] zone axes for SBA-16 cubic mesoporous silica containing sulfonic acid groups (20 mol% CSPTMS containing SBA-16 in the starting mixture).

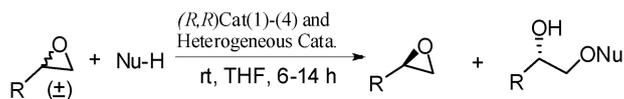
To observe the trends in the catalytic properties of new heterogeneous chiral salens, the ARO of racemic (\pm) epichlorohydrin (ECH) by nucleophiles such as water and phenol derivatives were examined. SBA-16 catalysts bearing sulfonic acid groups were used as a support to anchor the optically active salen complexes. The enantioselectivity of chiral cobalt-salen complexes anchored on the mesoporous materials were compared to those of homogeneous catalysts with a similar structure (cata 1 and 2 in Scheme 1). The homogeneous Co(III) salen catalysts containing MSA, CSA or NBSA anions (catalysts 1–4) showed a relatively high activity and enantioselectivity as shown in Table 2.

The chiral Co(III) salen complexes attached to propylsulfonic anion groups on SBA-16 exhibited remarkably high activity, and they could be employed at very low loadings to obtain the enantio-enriched products without suffering a solubility problem or severe deactivation. The HKR of (\pm)-ECH (entries 5, 6) and (\pm)-methyl-4-[(oxiran-2-yl)methoxy]benzene acetate (entries 9, 10) by using chiral salen catalysts led to optically pure (*S*)-epoxides (>98 ee%, >41% product yield). Significantly accelerated rates in the HKR or ARO reaction of racemic epoxides by nucleophiles were observed using a chiral Co(III)-SO₃ salen catalyst linked by arenesulfonic acid on SBA-16 in this work.

As another application on new reactions, the synthesis of chiral atenolol could be performed efficiently *via* ring opening of racemic ECH with methyl-*p*-hydroxyphenyl acetate as shown in Table 2. The reactions were completed within 12 h in good yields with promising enantioselectivities up to 98% ee (entries 14, 15) using our heterogeneous chiral (A), (B)/SBA-16 salen catalysts to produce optically pure (*R*)-methyl 2-(4-(3-chloro-2-hydroxypropoxy)phenyl) acetate (MCHPA). Transformation of chiral MCHPA into the chiral atenolol can be simply accomplished by an additional two-step treatment after HKR. The use of cobalt(III)-SO₃⁽⁻⁾ salen linked to

(A) Homogeneous Chiral Salen Catalysts**(B) Heterogenized Chiral Salen Catalysts****Scheme 1**

SBA-16 can avoid the necessity of catalyst separation by evaporation. Since this is a heterogeneous catalyst, it offers the practical advantages of facile separation and isolation of the catalyst from liquid products. The activity of recycled catalysts diminishes by 5% as compared to that obtained in the first run at the third reuse in HKR of ECH (same reaction as entries 5 and 6 in Table 2). This may be due to the dissociation of attached Co(III) salen from the supports in the presence of highly polar products such as 1-chloropropane-2,3-diol. However, high enantioselectivity (>98% ee) was obtained with prolonged reaction time. Further, the slightly deactivated catalysts could be recovered again by treatment

Table 2 Enantioselective ring opening of terminal epoxides catalyzed by chiral Co(III) salen complexes

Entry	Nu-H	R	Catalyst ^a	Loading ^b (mol%)	t/h	ee% of epoxide (yield, %) ^c
1	H ₂ O	CH ₂ Cl	Cata 1	0.5	9	95 (42)
2	H ₂ O	CH ₂ Cl	Cata 2	0.5	9	97 (45)
3	H ₂ O	CH ₂ Cl	Cata 3	0.5	9	98 (47)
4	H ₂ O	CH ₂ Cl	Cata 4	0.5	9	97 (46)
5	H ₂ O	CH ₂ Cl	Cata(A)/SBA-16	0.4	7	98 (44)
6	H ₂ O	CH ₂ Cl	Cata(B)/SBA-16	0.4	6	>98 (45)
7	H ₂ O		Cata(A)/SBA-16	0.6	10	>98 (43)
8	H ₂ O		Cata(B)/SBA-16	0.5	9	98 (41)
9		CH ₂ Cl	Cata 1	2.0	12	93 (41)
10		CH ₂ Cl	Cata 2	2.0	12	96 (43)
11		CH ₂ Cl	Cata 3	2.0	12	98 (46)
12		CH ₂ Cl	Cata(A)/SBA-16	1.5	12	>98 (44)
13		CH ₂ Cl	Cata(B)/SBA-16	1.5	10	98 (42)
14	Phenol	CH ₂ Cl	Cata(B)/SBA-16	1.0	12	98 (43)

^a The catalysts are shown in Scheme 1; Cata(A)/SBA-16 and Cata(B)/SBA-16 correspond to samples 2 and 4 of Table 1. ^b Catalyst loading is based on the Co unit. ^c ee% of product was analyzed by chiral GC and HPLC. The yield is based on mol% of reactant epoxides.

with additional Co(II) salen under air in toluene *via* reattachment of Co(III) salen as Co(III) to SO₃⁽⁻¹⁾ groups. In other reactions; especially ring opening of racemic ECH with phenol derivatives (entries 12–14), no significant dissociation of cobalt-salen complexes into solution was found during the repeated use of catalysts, with the high catalytic activity of the fresh catalyst being retained. The catalysts could be reused several times without further treatment after reaction in THF solvent without significant loss in activity. This means Co(III) salens are attached strongly and are stable during the reaction. In addition, to verify that some of the reaction was not caused by the contribution of dissolved homogeneous catalyst, the solid catalyst was removed from an incomplete reaction batch and the reaction was continued (the heterogeneous catalysts were filtered out at *ca.* 20, 55 and 80 ee%, respectively, in three different batches (for reaction 12). For each reaction, the reaction stopped and no increase of conversion was investigated.

In conclusion, we have demonstrated a simple procedure for the direct synthesis of SBA-16 mesoporous silica functionalized with alkyl and aromatic sulfonic groups. The formation of sulfonic groups was investigated with the enhanced mesoscopic ordering in replacing TEOS with MPTES or CSPTMS (<20 mol%). Also, the efficient new immobilization method

of monomeric chiral cobalt(III) salen to SO₃ group through propyl- or phenethyl-linkage by electrostatic interactions has been developed to yield catalytically active sites. On the basis of asymmetric catalysis, it is noteworthy that the chiral (salen) complexes obtained by the present procedure can be applied as active and effective recyclable catalysts for the ARO of terminal epoxides by nucleophiles such as water and phenol.

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