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Effects of Primary and Secondary Surface Groups in Enantioselective Catalysis Using Nanoporous Materials with Chiral Walls

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Abstract: Mesoporous materials are valuable supports for the immobilization of various molecular catalysts. Cases in which the performance of the catalyst improves after immobilization have seldom been reported, especially when it comes to enantioselective synthesis. Knowledge of how the presence of the support surface alters the properties of a bound catalyst is therefore very important. In the current article, a new periodically ordered mesoporous organosilica material (PMO) with walls exclusively made of a chiral building block is presented. The attachment of Al^{III} as a Lewis acid center to the chiral group furnishes the material with catalytic activity, for instance, for the asymmetric carbonyl ene reaction. Thus, the presented materials are valuable model systems for studying the effect of the chiral surface and also neighboring groups attached to the silanol groups in the network. It is reported that surface-bound Al^{III} exhibits significantly better performance (higher ee values) than an analogous molecular reference catalyst. Furthermore, it could be shown that the ee values increase even further when more bulky secondary groups are attached to the pore walls. Therefore, the main conclusion of the current report is that for cases in which steric conditions of a catalyst play a crucial role its immobilization inside a tailor-made mesoporous organosilica material is beneficial with respect to cooperative effects between the catalytic center and neighboring surface groups.

Introduction

Because of the biological preference for only one of the alternative enantiomers (L-amino acids and D-sugars), it is important that pharmaceutical products are associated directly with the ability to allocate them in an enantiomerically pure form. Enantioselective synthesis using molecular catalysts in the homogeneous phase has already reached a profound stage of development.[1] Because of the numerous advantages of catalysis operating in the heterogeneous mode, the immobilization of molecular compounds on suitable supports represents an important task. However, how an interface affects the properties of a molecular catalyst bound to it is still a matter of intense discussion.[2,3]

Because there are numerous possibilities to shape and also to modify the surface of silica, it is one of the most important support materials. For instance, mesoporous silica materials with periodically ordered pore systems such as MCM-41 and SBA-15 have become important model systems in catalytic research.[4,5] Chiral groups can be attached to the walls of mesoporous silica materials such as MCM-41 and SBA-15 via grafting,[6] with the condensation of terminal organosilanes $R^*Si(OR')_3$ ($R^* =$ a chiral organic group) with surface-bound silanol groups (Si−OH) resulting in stable Si−O−Si linkages.[7] Good examples exist for amino acids and short peptide sequences.[8] Aida et al. reported a different, very interesting method.[7,9] A triblock surfactant, the so-called lizard template containing an alkoxysilane headgroup covalently bound to an amino acid group attached to a long alkyl chain together with ~90% of a source for unmodified SiO_2, was employed for the one-pot synthesis of a mesoporous material with ordered porosity.[9] The inherent disadvantage of the described methods is that the porous materials contain the chiral entity only in minor amounts, typically in the range 5−15 mol %.[7] Therefore, it is a tempting idea to attach catalytically active species to surfaces that are chiral by themselves.[5]

An alternative approach exists to equip mesoporous silica materials with higher organic functionality content. Periodically

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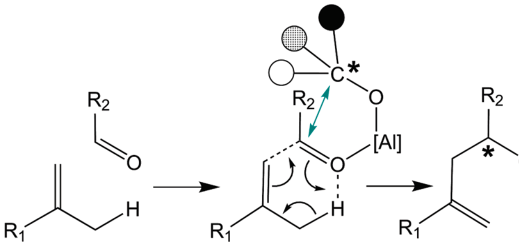
ordered mesoporous organosilica materials (PMOs) are prepared by pure and undiluted silsesquioxane precursors possessing a bridging organic group $(R'O)_3Si-R-Si(OR')_3$.[10] Because the composition of the resulting mesoporous network can be described as RSi_2O_3, the interfacial accessibility of the organic group is maximized.[11] The PMO field has been described recently in excellent review articles.[7,12]

There are a number of papers in which a sol−gel precursor containing a bridging, chiral entity in addition to a pure silica source (e.g., tetraethoxysilane) has been used for the preparation of mesoporous materials. Those materials were also frequently investigated in catalysis. For instance, Corma et al. have reported in several papers materials containing a chiral bridging vanadyl salen complex.[13] Li et al. have used a similar system containing a Mn(salen) complex and have reported several catalytic studies.[14] Garcia and Ihmels describe the stereoselective di-π-methane rearrangement in a mesoporous material containing a chiral 1,2-bis-(ureido)-cyclohexyl linker. Because in the latter reports the chiral entity has been introduced via co-condensation, it still represents the minor constituent with the majority of the materials consisting of SiO_2. Therefore, it can be envisioned that materials made exclusively from chiral building blocks are very interesting targets.

Examples of real PMOs (∼100% organic modification) where chiral building block have been used are still rare.[3] Our group applied enantioselective catalytic hydroboration to precursor $(EtO)_3Si-CH{=}CH-Si(EtO)_3$, resulting in a chiral PMO with $Si-C^*H(OH)-CH_2-Si$ entities embedded in the walls.[15] Later, Thomas et al. used a chiral hydroboration agent directly instead of a stereoselective catalyst.[16] The report of a PMO material containing a chiral amino acid entity was published in 2008, and for the first time the chirality of the surface was probed using physisorption measurements with a chiral gas.[17] Froeba et al. prepared a PMO with chiral benzylic ether bridges from enantioselective catalysis in 88% ee.[18] An entirely different and very interesting system was published by Crudden et al.[19] They prepared PMO materials containing a building block with axial chirality. To the best of our knowledge, there is currently no report on the application of a real PMO material with chiral walls in enantioselective catalysis.[20]

Asymmetric heterogeneous catalysis is a topic of immense interest. Therefore, it is not surprising that besides mesoporous solids with regular pore systems a variety of alternative materials have also been used for the immobilization of molecular catalysts. The discussion of the entire field is beyond the scope of this article. The interested reader is referred to the extensive review written by Glorius et al.[21] In comparison to other materials such as functional polymers, it can be expected that chiral PMOs are favorable because of the combination of the high density of the asymmetric groups and the possibility of assembling these groups with geometrical precision.[22] A complementary class of materials with pores in the micropore regime ($D_p < 2$ nm) should be noted as well: the so-called homochiral, porous metal−organic framework materials.[23]

Chart 1. Asymetric Carbonyle ene Reaction[24]



There are various reactions that are suitable as model reactions for enantioselective catalysis. The ene reaction is a little-known C−C coupling reaction. Its bandwidth ranges from cyclizations to ring-opening reactions, or decarboxylations. Its main characteristic is the addition of a C═X bond (the so-called eneophile) to a C═C bond possessing an allylic hydrogen (Chart 1). The ene reaction belongs to the class of pericyclic reactions and can be catalyzed by Lewis acids activating the C═X group. Al^{III} or Ti^{IV} alkoxo complexes can be used as suitable Lewis acids. Depending on the kind of substituents, a new stereocenter is generated, and it has been reported that the use of chiral, molecular catalysts allows enantioselective synthesis.[24] For instance, (−)-menthol is produced industrially using the intramolecular ene reaction. Inspired by this work, we attempt to synthesize a corresponding catalytic system based on a PMO material.

Results and Discussion

Very recently, our group described a versatile PMO precursor: 1,3-bis-tri-iso-propoxysilyl-5-bromobenzene (**1**).[25] It could be shown that the derivatization chemistry known for halogenated aromatic compounds can also be applied in the case of **1**.[26] As a consequence, the so-called UKON-PMO materials with organosilicate networks constructed from benzoic acid, dithiobenzoic acid, aniline, and others have been described recently.[17,22,25,27] Here, a new mesoporous organosilica with chiral pore walls is reported. (See Chart 2; more details are given in the Experimental Section.) The lithiation of **1** at the 5-position leads to a versatile nucleophilic species that can attack the carbonyl species in acetone, resulting in the racemic (1-

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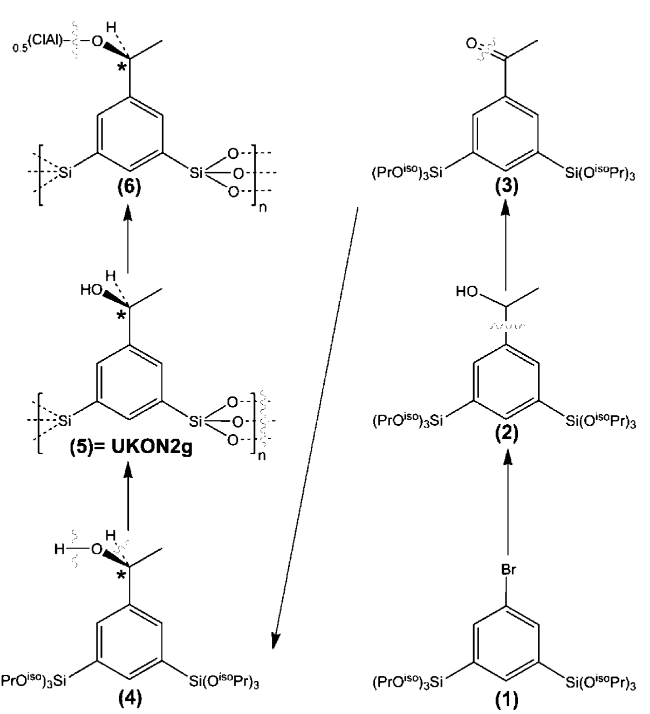
Chart 2. Synthesis Steps Leading to the New Mesoporous Organosilica Material with Chiral Pore Walls[a]



[a] Retrosynthesis considerations are indicated by the wavy gray lines.

hydroxyethyl)benzene derivative (**2**). The oxidation of **2** using pyridinium chlorochromate affords the acetophenone derivative (**3**). Finally, the enantioselective hydroboration[28] of the C═O bond results in novel, chiral sol−gel precursor (−)-(*S*)-1,3-bis-tri-iso-propoxysilyl-5-phenylethanol (**4**).

Each of the compounds (**1**−**4**) has been purified prior to use in a succeeding step and was characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy and mass spectometry (MS). The latter data are given in the experimental section. Because of the chirality of **4**, some additional analytical techniques became necessary. **4** is optically active ($\alpha_D = -8.4°$), and its CD spectrum is shown in Figure 1d. In addition, the success of the enantioselective hydroboration reaction could be probed quantitatively. **4** was reacted with a chiral shift reagent (Supporting Information SI-1) followed by ^{31}P NMR spectroscopic evaluation.[29] The relative intensities of the two ^{31}P NMR signals ($\delta_1 = 149.25$ ppm and $\delta_1 = 142.73$ ppm) allows us to determine the abundance of the two possible enantiomers. For the reaction of **3** to **4**, an ee value of 98% has been determined. Chemically analogous but racemic compound **2** was taken as a reference. Expectedly, the ee value for the formation of **2** from **1** was 0%.

New mesoporous organosilica material UKON2g was prepared from **4** using amphiphilic block copolymer Pluronic P123 as a structure-directing agent at low pH (= 0) under true liquid-crystal conditions.[30] The resulting material was characterized by a variety of analytical methods including transmission electron microscopy (TEM, Figure 1a), N$_2$ physisorption (Figure 1b), small-angle X-ray scattering (SAXS, Figure 1c), solid-state ^{13}C- (SI-2) and ^{29}Si- (Figure 2b) NMR spectroscopy, and FT-IR (SI-2) and CD spectroscopy (Figure 1d). A mesoporous material with a cylindrical pore-system has formed as indicated by TEM. The pore-to-pore distance is $d_{100} = 11.8$ nm according to SAXS. Because only one diffraction peak is seen in SAXS, it can be concluded that only parts of the sample are highly ordered. The isotherm of UKON2g possesses a shape that is typical for mesoporous solids with a capillary condensation step at $p/p_0 \approx 0.63$.[31] The material possesses an internal surface area of 1045 m^2/g as determined by the BET method.[32] The high amount of adsorbed gas in the pressure range below $p/p_0 < 0.06$ and the steady increase for pressures lower than $p/p_0 = 0.4$ indicates the presence of large micropores. The pore-size distribution function of UKON2g was determined from the BJH evaluation of the adsorption branch of the isotherm.[33] A pore-size maximum at $D_P = 5.3$ nm is found (Figure 1b). The pore-size determined from N$_2$ physisorption is in good agreement with the TEM data. In combination with the SAXS data, it can be estimated that the pore walls of UKON2g are relatively thick ($D_{\text{thickness}} \approx d_{100}(\text{SAXS}) - D_{\text{pore}}(\text{N}_2) \approx 6.5$ nm). The latter finding can also be confirmed by TEM images. It is seen that the pore walls have extensions that are similar to those of the pores (Figures 1a and SI-2). The chemical nature of UKON2g was investigated via solid-state MAS NMR spectroscopy. The ^{29}Si NMR spectrum of UKON2g (shown in Figure 2b) contains three signals characteristic of organically modified silica materials at $\delta = -69$ ppm for (HO)$_2$R*Si*(OSi) $\cong$ T^1, −78 ppm for (HO)R*Si*(OSi)$_2$ $\cong$ T^2, and −87 ppm for R*Si*(OSi)$_3$ $\cong$ T^3.[34] Signals indicating the presence of pure silica (SiO$_2$; so-called Q signals at $\delta \approx -110$ ppm) are not seen. This proves that the precursor has been used in an undiluted form and that the Si−C bonds in UKON2g are stable. In the ^{13}C NMR spectrum, the signals for $C^hH_3C^gH(OH)PhSi_2O_3$ ($\delta^g = 72.2$ ppm, $\delta^h = 26.0$ ppm) and the remaining C$_{\text{arom}}$ ($\delta = 134.6$, 142.3, and 148.4 ppm) are observed (SI-2). It was determined qualitatively via CD spectroscopy that the stereochemical information was maintained during the transition of the precursor (**4**) to the material (**5**). It is important to note that CD spectroscopy applied to solid materials is very susceptible to artifacts due to scattering or insufficient transmission. Thus, a thin film of the UKON2g mesoporous organosilica material has been prepared via spin coating (Experimental Section). Still, one has to be careful with the thickness and homogeneity of the film. Data suitable for a qualitative comparison of the precursor (**4**) and the resulting chiral mesoporous organosilica materials could be obtained for a film of 50 nm thickness (Figure 1d). An amplitude to negative rotational angles ($\lambda = 240-200$ nm) and a band with a negative sign at $\lambda \approx 205-207$ nm is seen for both compounds, the precursor and the resulting mesoporous organosilica material.

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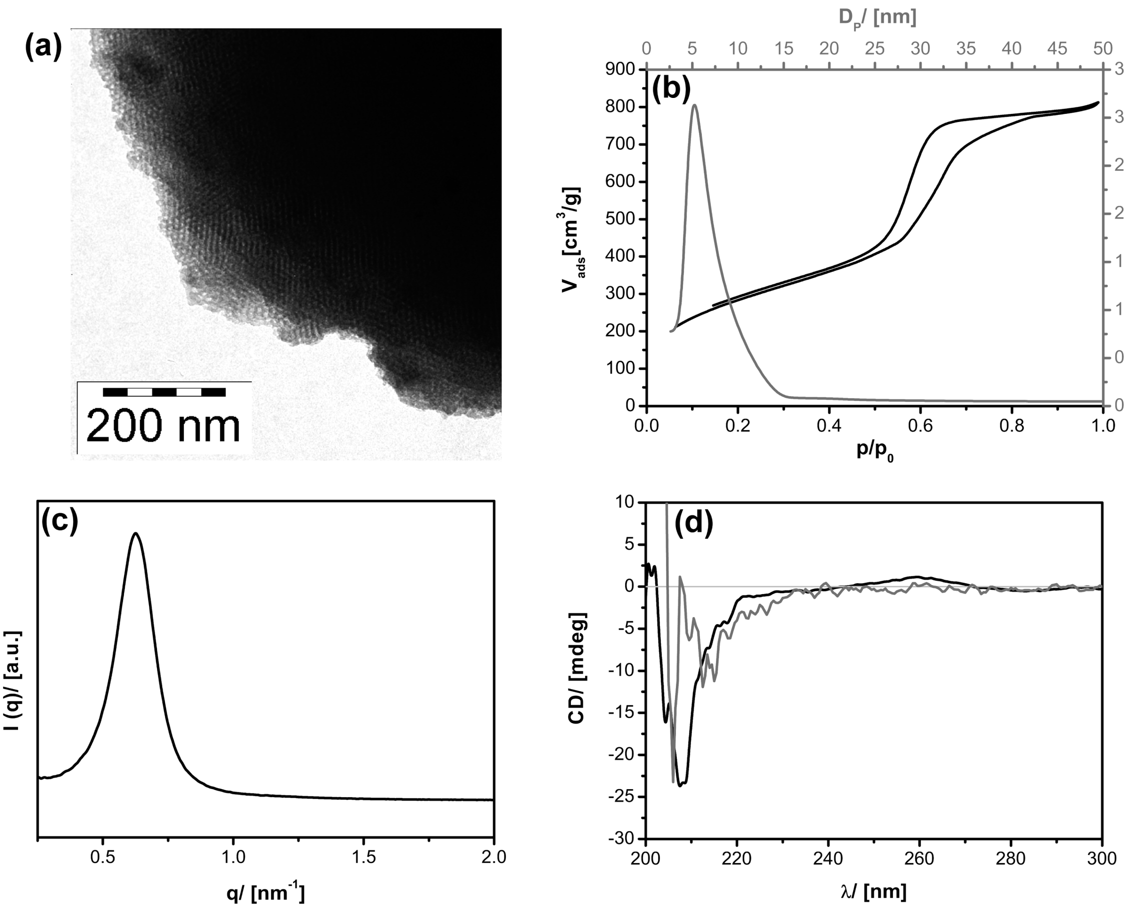


Figure 1. Selected analytical data for the new chiral, mesoporous organosilica material UKON2g. (a) TEM micrograph, (b) N_2 phyisorption isotherm (black) and BJH pore-size distribution function (gray), (c) SAXS, and (d) CD spectrum (gray) in comparison to the spectrum of the precursor (**4**, black) as a reference.

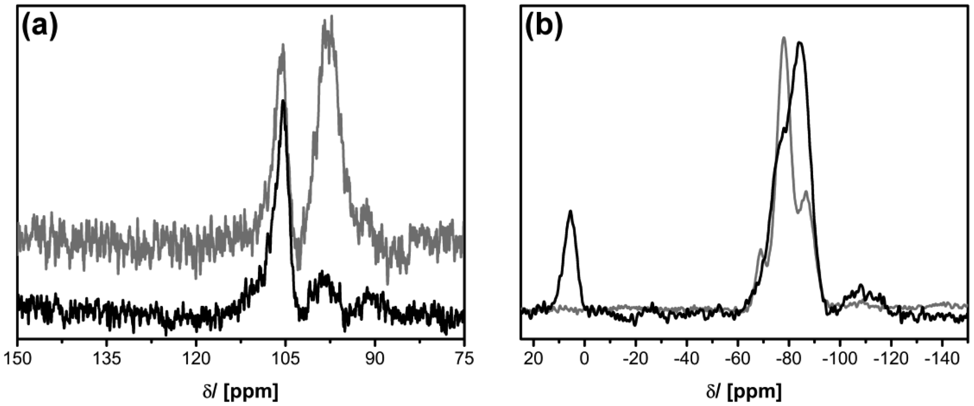
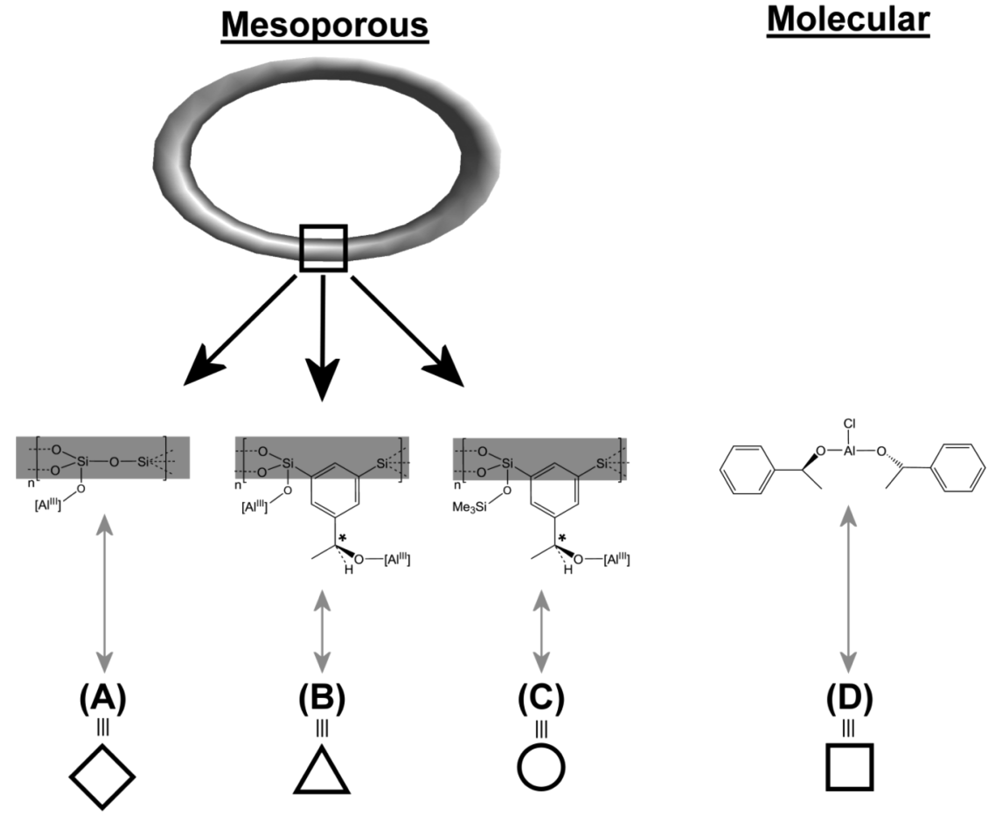


Figure 2. (a) ^{27}Al and (b) ^{29}Si solid-state NMR spectra of the materials obtained after Me_2AlCl treatment of the as-prepared UKON2g (gray curves) in comparison to that of materials with silanol groups quenched by silylation.

The attachment of the Lewis acid Al^{III} to the chiral alcohol group could be achieved via treatment of UKON2g with Me_2AlCl (Experimental Section). However, the problem was encountered that Me_2AlCl also reacts readily with surface silanol groups as proven by the solid-state ^{27}Al NMR spectra shown in Figure 2a. Two signals of comparable intensity are present at $\delta = 105.4$ ppm corresponding to *Al*−O−C* and at $\delta = 97.9$ ppm corresponding to the undesired *Al*−O−Si species. The latter material is denoted as catalytic material (B) in the following parts of the article (Scheme 1). Quenching of the silanol groups in UKON2g could be achieved after its treatment with a silylation reagent such as R_3SiCl (R = Me, Experimental Section). It is important to note that the silylation reagent will also initially react with the alcohol groups. However, the resulting C−O−$SiMe_3$ motif, which is also known as a protecting group, can be easily reconverted to C−OH via treatment with trifluoroacetic acid (Experimental Section). As a result, it can be seen in the solid-state ^{29}Si NMR spectra (Figure 2b) that one new signal at $\delta = 5.4$ emerges that is typical of Si−O−*Si*Me_3. The treatment with trifluoroacetic acid has one slight disadvantage. A small signal at −110 ppm has appeared in the ^{29}Si spectrum of the material after silylation (Figure 2b).

Scheme 1. Different Catalytic Systems Used in This Study



This signal is typical of so-called Q-type silicon atoms ($(HO)_{4-x}Si(OSi)_x$) and can be explained by the minor cleavage of the Si−C bond by traces of fluoride ions known to be dissolved in trifluoroacetic acid. When silylated UKON2g is treated with Me_2AlCl, one obtains material **C**. It can be seen clearly from the ^{27}Al NMR spectrum that the undesired species Al−O−Si has almost vanished. The majority of Al^{III} centers are attached to the asymmetric center via an oxo bridge (Scheme 1) in material **C**. In addition to materials **C** and **B**, a purely siliceous SBA-15-type mesoporous material treated analogously with Me_2AlCl (denoted as material **A**) and a corresponding chiral molecular compound **D** were used as reference catalysts in the asymmetric carbonyl ene reaction (R_1 = phenyl, R_2 = CCl_3; see Chart 1). The reaction mixtures were investigated by NMR spectroscopy (SI-3). The results of studies with four catalytic systems A−D are shown in Figure 3. Depending on reaction conditions, in addition to the signals corresponding to the ene product, the presence of minor amounts of the starting compounds and a byproduct originating from the oligomerization of styrene has been observed. It is important to note that the ene reaction may proceed according to three different mechanisms (SI-4): a concerted mechanism involving a 6π aromatic system, a zwitterionic mechanism, and a radical mechanism. The latter process is obviously responsible for the oligomerization of styrene, and indeed oligomeric α-methyl styrene species could be identified as the byproduct by ^{1}H NMR spectroscopy (SI-3).

A is clearly the inferior catalyst in the discussed series (Figure 3; hashes). Only a relatively low amount of the ene product in its racemic form has formed at room temperature (RT). Instead, much of the byproduct is present. The performances of the alternative catalysts (**C** and **D**) at RT are very similar to each other. On the order of 80% of the ene product has formed. Unfortunately, there is practically no stereochemical differentiation (ee values ≈ 0). However, significant differences between the three catalytic systems containing the chiral Al species can be observed at temperatures below 0 °C. In the case of catalyst **B**, it has been found that the yield of the ene product drops quickly with temperature and at the same time more of the byproduct forms (Figure 3a,b). Considering the latter findings together with the results reported for catalyst **A**, it can be concluded that the Al^{III} species attached to silanol groups is responsible for the formation of the undesired byproduct. The latter assumption is supported by the fact that the molecular reference catalyst (**D**) and the silanol-protected material (**C**) show almost the same temperature dependency regarding the yield of the ene product (Figure 3a; squares and spheres). The question arises as to if there are differences in stereochemical effects (Figure 3c). The stereochemical differentiation increases when the temperature is lowered. Although the ee value at $T = -55$ °C is 72% in the case of catalytic material **C**, it is only 17% for molecular reference catalyst **B**. The 4-fold increase in enantioselectivity simply due to immobilization is remarkable and requires further explanation.

The stereochemical control in enantioselective catalysis is the result of a complex interplay of the electronic and steric influences of the ligands and the metal center to which they coordinate. It has been observed very frequently that the steric demand of the chiral group at the catalyst enhances the stereochemical control (Chart 1).[35] Therefore, it can be assumed that the presence of the pore surface increases the steric constraints in comparison to a molecular system. Two approaches are proposed for changing such steric constraints even further (Figure 4). It is envisioned that the mobility of guests

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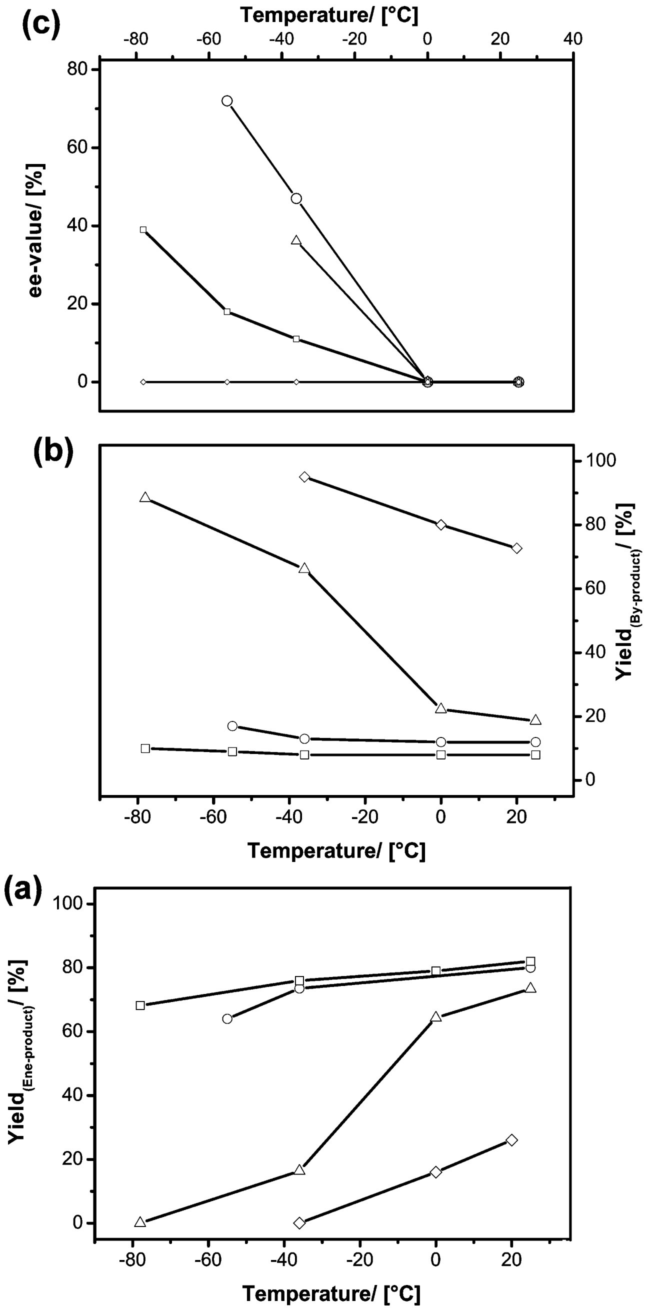

Figure 3. Relative yield of the ene product (a, black curves), yield of the byproduct (b, gray curves), and enantioremic excess (c, black curves) for four different catalytic systems: **C** (○), **B** (△), molecular catalyst **D** (□), and **A** (hashes). See also Scheme 1.

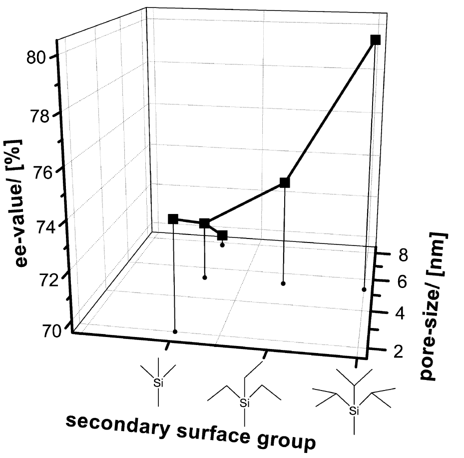

Figure 4. Dependence of the ee value on the pore size and character of the secondary surface group.

inside the pores is restricted when the pores become smaller. This in turn could influence the ee values. Three materials with pore sizes of $D_p \approx 2$, 5.3, and 7.8 nm were prepared (Experimental Section and SI-5), the surface silanol groups of all three materials were modified with the same group ($O-SiMe_3$), and the catalytic tests were performed at the same temperature ($T = -55$ °C). The dependence of the ee value on pore size could be observed (Figure 4), but the effect is not very pronounced ($ee_{7.8\ nm} = 70\%$, $ee_{5.3\ nm} = 72\%$, and $ee_{2\ nm} = 74\%$). Therefore, a second approach was attempted. Instead of the modification of the free silanol groups with $O-Si(Me)_3$, the more bulky $O-Si(Et)_3$ and $O-Si(^{iso}Pr)_3$ functionalities were attached. This time the pore size of the materials ($D_p = 5.3$ nm) was kept constant. It can be seen (Figure 4) that the secondary $O-SiR_3$ groups attached to the surfaces of the organosilica mesopores have a profound impact on the enantioselectivity of the catalytic reaction. The ee values increase in the order of $R = $ Me (72%) < Et (74%) < ^{iso}Pr (80%). For the explanation of this effect, one has to consider the effect of the molecular structure of the surface on the transition state of the ene reaction involving a six-membered ring as depicted in Chart 1. A model of the organosilica surface derived from molecular mechanics calculations is shown in Figure 5. It can be seen that the presence of the secondary surface groups mainly affects the rotational freedom of the Al−O contact formed between the Lewis acid Al^{III} center and the carbonyl compound. If the surfaces are modified by $O-Si^{iso}Pr_3$, then this rotation is strongly hindered and the position of the emerging stereocenter is fixed in the vicinity of the asymmetric carbon atom of the organosilica surface. However, for the less bulky $O-SiMe_3$ it is clear that the rotation is much less hindered. It is reasonable that the stereochemical influence of the chiral center attached to Al^{III} via the alkoxide C^*-O-Al function is less pronounded when the probability of the emerging stereocenter in the vicinity decreases because of rotation (Figure 5). The discussed picture would also explain the observed temperature dependence of the enantioselectivity for catalytic systems **B** and **C**.

Conclusions

In the present work, the synthesis of a new, periodically ordered mesoporous organosilica material with a chiral surface was described. Because the surface contains chiral secondary alcohol functions, the modification with Al^{III} was successful when surface silanol groups were masked as silyl-esters. One possible application of this material as a catalyst in the asymmetric ene reaction was investigated. The enantioselectivity of the described system is much higher than for an analogous molecular reference catalyst in the homogeneous case.

The latter results points to a more general testimony of the current article. In several reports in the past, molecular catalysts that had already been characterized by high ee values were the targets of an immobilization strategy. The findings reported here indicate that better stereochemical control can be achieved even for less-appropriate ligands when the catalyst is imbedded into the walls of a mesoporous solid. Better stereochemical control can also be achieved even for less-appropriate ligands when the chiral ligand is imbedded into the walls of a mesoporous solid. In this sense, the surface behaves as a bulky ligand. The

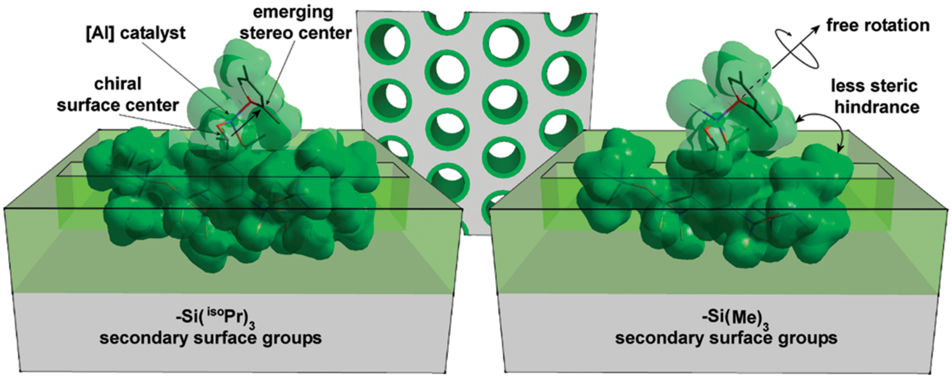

Figure 5. Schematic image indicating the cooperative effect between the Al^{III} catalyst attached to the chiral surface center and the secondary surface groups. A transition state such as that shown in Chart 1 has been assumed.

latter hypothesis is supported by the fact that achiral secondary groups on the surfaces (here the silyl-ester groups) have a direct effect on the enantioselectivity of the reaction. A cooperative effect between the catalytically active entity and the secondary surface groups could be proven.

Experimental Section

General Comments. Starting compounds were received from Sigma-Aldrich and were purified and dried prior to use. All reactions on the precursor state were performed with the exclusion of air and moisture using the Schlenck technique. Special caution needs to be exercised when working with alkylated lithium compounds because of their spontaneous ignition in air.

Synthesis. 1,3-Bis-tri-iso-propoxysilyl-5-bromobenzene (**1**) was prepared according to the literature.[25]

1-(3,5-Bis-tri-iso-propoxysilylphenyl)-ethanol (2). ^{tert}BuLi (1.5 M, 3.5 mL, 5.3 mmol) is added dropwise to a solution of **1** (1.5 g, 2.65 mmol) in 50 mL of dry Et_2O at $T = -78$ °C. The mixture is stirred for 30 min, followed by the addition of acetaldehyde (0.26 g, 5.4 mmol). After the mixture is warmed to room temperature, the solvent is removed under vacuum. Dry pentane (60 mL) is added. The nonsoluble residue is removed via centrifugation. Finally, the product (**2**) (0.84 g, 1.59 mmol, yield 60%) is isolated by column chromatography (silica gel 60, hexane/AcOEt 10/1 → 2/1) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (d, 36 H, $^3J = 6.1$ Hz, $CH(CH_3)_2$), 1.47 (d, 3H, $^3J = 6.4$ Hz, $CHCH_3$), 4.25 (sept, 6H, $^3J = 6.1$ Hz, $O-CH(CH_3)_2$), 4.89 (q, 1H, $^3J = 6.4$ Hz, $CHCH_3$), 7.72 (m, 2H, o-arom H), 7.92 (t, 1H, $^4J = 1,2$ Hz, p-arom H). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 25.0 ($CHCH_3$), 25.4 ($CH(CH_3)_2$), 65.6 ($O-CH(CH_3)_2$), 70.5 ($OCH-CH_3$), 131.9 (C-arom C), 133.6 (Si-arom C), 140.8 (o-arom C), 143.7 (p-arom C). IR (ATR) ν: 1040 (Si−O), 1111 (C−O), 1369−1467 (aliph + arom C−C), 2894−2972 (aliph + arom C−H), 3421 (O−H) cm^{-1}. EI-MS (70 eV): m/z = 529 (M^+), 514 (−Me), 471 (−O^{iso}Pr), 205 (Si(O^{iso}Pr)$_3$).

1-(3,5-Bis-tri-iso-propoxysilylphenyl)-ethanone (3). Pyridinium chlorochromate (0.24 g, 1.33 mmol) is dissolved in dry CH_2Cl_2 (15 mL), and **2** (0.4 g, 0.76 mmol) is added. The mixture is stirred at room temperature for 4 h while the color changes from orange to dark brown. After the removal of the solvent in vacuum, the product is purified via column chromatography (silica gel 60, 1. CH_2Cl_2; 2. AcOEt). The product (**3**) (0.322 g, 0.608 mmol, yield 80%) is isolated as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.15 (d, 36H, $^3J = 6.1$ Hz, $CH(CH_3)_2$), 2.54 (s, 3H, $CHCH_3$), 4.21 (sept, 6H, $^3J = 6,1$ Hz, $O-CH(CH_3)_2$), 8.13 (s, 1H, p-arom H), 8.24 (s, 2H, o-arom H). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 25.6 ($CH(CH_3)_2$), 26.7 ($CH(CH_3)_2$), 65.7 ($O-CH(CH_3)_2$), 132.0, 135.6, 136.4, 146.1 (arom C), 198.5 (C═O). IR (ATR) ν: 1013 (Si−O), 1116 (C−O), 1354−1369 (aliph + arom C−C), 1690 (C═O), 2890−2972 (aliph + arom C−H) cm^{-1}.

(−)-1-(3,5-Bis-tri-isopropoxysilyphenyl)-ethanol (4). A solution of (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol (0.29 g; 2.0 mmol) and trimethyl borate (0.21 g, 2.0 mmol) in 2 mL of THF is prepared at room temperature. The mixture is stirred for 30 min, and the solvent is removed under vacuum. Two milliliters of THF are added again, and 0.18 mL of this solution is used as a catalyst in the next step. **3** (0.38 g, 0.72 mmol) and the catalyst are dissolved in 3 mL of THF and cooled to 0 °C. The solution is stirred for 15 min, and $BH_3 \cdot DMS$ (2 M, 0.4 mL, 0.8 mmol) is added drop by drop. Afterwards, the light-yellow solution is stirred for 48 h at RT. The solvent is removed in vacuum, and the product (**4**) (0.34 g, 0.65 mmol, yield 90%) is isolated via column chromatography (silica gel 60, PE/EE 3/1) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (d, 36H, $^3J = 6.1$ Hz, $O-CH-CH_3)_2$), 1.45 (d, 3H, $^3J = 6.4$ Hz, sec-alk CH_3), 4.24 (sept, 6H, $^3J = 6.1$ Hz, $O-CH-(CH_3)_2$), 4.87 (q, 1H, $^3J = 6.4$ Hz, sec-alk CH), 7.65 (s, 2H, o-arom H), 7.91 (s, 1H, p-arom H). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 24.1 (alk CH_3), 24.5 ($O-CH-(CH_3)_2$), 64.4 ($O-CH-(CH_3)_2$), 69.4 (alk CH), 131.0, 132.7, 139.8, 142.9 (arom. C). IR (ATR) ν: 1040 (Si−O), 1112 (Si−C), 1369−1467 (aliph + arom C−C), 2894−2972 (aliph + arom C−H), 3421 (O−H) cm^{-1}. EI-MS (70 eV) m/z: 529 (M^+), 514 (−Me), 471 (−OiPr), 205 (Si(OiPr)$_3$). Determination of ee value: **4** (0.05 g, 0.095 mmol) is dissolved in a mixture of $CDCl_3$ (0.2 mL) and triethylamine (0.1 mL). Afterwards, a solution of PCl@(*R*)-(+)-1,1′-bi-2-naphtol (0.033 g, 0.095 mmol) in $CDCl_3$ (0.2 mL) is added drop by drop. The reaction mixture is stirred for 30 min, and a ^{31}P NMR spectrum is recorded. See also SI-1. ^{31}P NMR (161.98 MHz, $CDCl_3$) δ: 142.9 (+ enantiomer); 149.8 (− enantiomer).

Mesoporous Organosilica Material UKON2g (5.3 nm Pore Size) (5). The sol−gel precursor (**4**) (0.45 g, 0.88 mmol) and Pluronic P-123 (0.26 g) are dissolved in ethanol (1.2 g). Aqueous HCl (1 M, 0.26 g) is added drop by drop while stirring. The sols are aged in an open container for around 1 week. The resulting monolithic pieces are dried in vacuum at 100 °C for 24 h. The template is removed by extraction with EtOH (25 mL) and aqueous HCl (25 mL) at $T = 45$ °C. Complete removal of the block copolymer occurs within 2−4 days. ^{13}C MAS NMR (100.61 MHz, cptoss, 6 kHz) δ: 25.5 (CH_3-sec alkohol), 70.3 (CH-sec alkohol), 131, 138, 144 (arom C). ^{29}Si-MAS NMR (79.5 MHz, cp, 6 kHz): δ −78.5 (typical T-type signals). IR (ATR) ν: 1058 (Si−O + Si−C), 2881−2980 (aliph + arom C−H), 1264−1446 (aliph + arom C−C), 3300 (OH) cm^{-1}. N_2 physisorption: BET surface area =1045 m^2/g; BJH pore diameter = 5.3 nm. SAXS ($P = 4$ kW, Cu Kα): $q_{100} = 0.63$ nm^{-1}.

UKON2g with 2 nm Pore Size. Materials were prepared according to the literature using β-methyl-cyclodextrine (0.26 g) as a template.[36]

UKON2g with 7.8 nm Pore Size. A mixture of Pluronic P-123 (0.26 g) and 1,3,5-trimethylbenzene (0.125 g) is used as a template phase.

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(36) Polarz, S.; Smarsly, B.; Bronstein, L.; Antonietti, M. *Angew. Chem., Int. Edit.* **2001**, *40*, 4417.

Thins Films of UKON2g. The sol used for the preparation of UKON2g was aged for 24 h. One drop was spin coated onto a thoroughly cleaned quartz slide (2.5×2.5 cm^2) using a spin coater from LOT (model SCV-10) at a rotational speed of 5000 min^{-1}. The coated quartz substrates were then transferred into an atmospheric chamber at $T = 40$ °C and room humidity $R = 50\%$. After the condensation of the silica film, the material was dried at 100 °C and then used for CD measurements. The template was not removed, and the films were checked regarding their thickness and homogeneity using scanning electron microscopy (SEM). Further characterization was not done.

Quenching of Silanol Groups in UKON2g. The modification with $SiMe_3$ is discussed as a representative case. The modification with alternative groups SiR_3 (R = Et, ^{iso}Pr) has been performed in an analogous way. UKON2g (0.2 g, 0.91 mmol) is dried in vacuum at 100°. Solvent $Me_3Si{-}O{-}SiMe_3$ (7.5 g) and Me_3SiCl (5 g, 46.1 mmol) are added. The mixture is heated to reflux for 15 h, and the solid material is separated via centrifugation. To remove the remaining $Me_3Si{-}O{-}SiMe_3$ and Me_3SiCl from the pore system, the material is stirred in 40 mL of dry THF, followed by centrifugation and drying in vacuum at 100 °C. To remove Me_3Si groups from the alcohol function, the material is stirred in 20 mL of EtOH and 20 mL of trifluoroacetic acid for 15 h. Afterwards, the material is isolated via centrifugation and dried in vacuum at 100 °C.

Modification of UKON-2g with Al^{III}. Mesoporous organosilica material UKON2g (0.2 g, 0.91 mmol) is dried in vacuum at 100 °C. The material is cooled to −78 °C, and $AlMe_2Cl$ (1 M in hexane, 5 mL, 5 mmol) is added. The reaction proceeds for 24 h at RT. Then, the solid material is isolated by centrifugation. To remove unreacted residues of $AlMe_2Cl$ from the pore system, the material is stirred three times for 24 h in 60 mL of dry pentane. Finally, the resulting material is dried in vacuum at 80 °C and stored under inert conditions inside a glovebox.

Catalytic Tests. $CDCl_3$ (0.5 mL) as a solvent and chlorale (0.2 g, 1.36 mmol) are added to the Al^{III}-modified mesoporous organosilica material (**6**) (30 mg). The mixture is cooled to −36 °C, and α-methylstryrene (0.16 g; 1.36 mmol) is added drop by drop. The reaction mixture is stirred for 24 h at different temperatures, and the catalyst is filtered off. The products of the reaction are studied by NMR spectroscopy. The results of the catalytic tests are summarized in Table 1 shown in SI-6.

Determination of ee Values. To 0.3 mL of the reaction mixture from the asymmertric ene reaction is added 0.1 mL of triethylamine. Afterwards, a solution of 0.033 g of PCl@(*R*)-(+)-1,1′-bi-2-naphtol (0.095 mmol) dissolved in 0.2 mL $CDCl_3$ is added drop by drop. The reaction mixture is stirred for 30 min, and a ^{31}P NMR spectrum is recorded. ^{31}P NMR (161.97 MHz, $CDCl_3$, determination of ee) δ 150.95 ⇒ (+) - enantiomer; δ 153.35 ⇒ (−) - enantiomer.

Analytical Methods. NMR spectra were acquired on a Varian Unity INOVA 400 spectrometer using dried $CDCl_3$ as a solvent. Solid-state NMR spectra were recorded using a Bruker DRX 400 spectrometer. The following experimental parameters were used for the measurements. ^{13}C: We used a cross-polarization pulse program, a spin rate of 6 kHz, a 5 s recycle delay, a 2 ms contact time, and a $\pi/2$ pulse width of 6.2 μs. ^{29}Si: We used a cross-polarization pulse program, a spin rate of 6 kHz, a 40 s recycle delay, a 12 ms contact time, and a $\pi/6$ pulse width of 2.2 μs. The TEM images were performed on a Zeiss Libra 120 at 120 kV acceleration voltage. The TEM samples were prepared by quickly dipping a carrier covered with a holey carbon foil (Plano company, S147) in the solution, where the ground UKON materials were dispersed in THF. FT-IR spectra were recorded by using a Perkin-Elmer Spectrum 100 spectrometer with an ATR unit. Small-angle X-ray scattering (SAXS) measurements were conducted with a Bruker AXS Nanostar. N_2 physisorption measurements were recorded on a Micromeritics Tristar. CD spectra were obtained on a Jasco J-715 instrument.

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Supporting Information Available: ^{31}P NMR investigation of **4** in comparison to racemic **2** using a chiral NMR shift reagent. Additional analytical data for chiral mesoporous organosilica material UKON2g. Investigation of the catalyzed carbonyl ene reaction with ^1H NMR spectroscopy. Different possibilities for the mechanism of the ene reaction. N_2 physisorption measurements of chiral mesoporous organosilica material UKON2g with two additional pore sizes. Summarized catalytic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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