Polymer Fibers as Carriers for Homogeneous Catalysts

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Abstract: This paper describes a polymer fiber-based approach for the immobilization of homogeneous catalysts. The goal is to generate products that are free of catalysts which would be of great importance for the development of optoelectronic or pharmaceutical compounds. Electrospinning was employed to prepare the non-woven fiber assembly composed of polystyrene. The homogeneous catalyst scandium triflate was immobilized on the polystyrene fibers during electrospinning and on corresponding core shell fibers using a fiber template approach. An imino aldol and an aza-Diels–Alder model reaction were carried out with each fibrous catalytic system. This resulted in the immobilization of homogeneous catalysts in a polymer environment without loss of their catalytic activity and may even be enhanced when compared with reactions carried out in homogeneous solutions.

Keywords: homogeneous catalysis · immobilization · polymers · scandium

Introduction

Homogeneous catalysis, although highly successful in a broad range of chemical reactions, is often problematic due to the fact that the catalyst is homogeneously mixed on a molecular scale within the reaction mixtures. Separation of the catalysts from the product is difficult and this is a particularly significant problem in the synthesis of pharmaceutical, electronic or optoelectronic compounds which should ideally be completely free of catalysts. Furthermore, as one goes from batch reactions to continuous reactions—microreaction techniques being examples in case—one faces the problem of keeping the catalyst in the reaction vessel while the reaction components are pumped through.[1] Finally the possibility to re-use homogeneous catalysts as often as possible is an issue of economic importance.

The concept of immobilizing a catalyst which originates from heterogeneous catalysis seems to offer a partial solution to this problem. In heterogeneous catalysis, catalysts have been immobilized on porous carriers including zeolites, porous aluminum oxide particles, titanium dioxide and graphite with great success.[2,3] Immobilization on porous substrates allows one to control the specific surface area, the accessibility of the catalyst and even its catalytic activity in cases where the electronic state of the catalyst is modified as a result of its contact with the materials used for immobilization. A further advantage is that immobilization frequently allows the retrieval of the catalyst from the reaction mixture at very high percentages.

An alternative approach involves the immobilization of homogeneous catalysts by attachment to a support via coordinate or covalent bonds.[4] However, this approach has been found to frequently reduce the effectiveness of the catalyst to a significant degree. In any case, this type of concept which originates from heterogeneous catalysis seems to be in contrary to the intrinsic nature of homogeneous catalysis to a certain extent, that is, a molecular dispersion within the reaction mixture, in general in solution or melt. This does not, however, imply that carriers can not be used in homogeneous catalysis in a stricter sense. The molecular dispersion of a homogeneous catalyst within a carrier should not really restrict the catalytic activity of a given homogeneous catalyst. In other words, the components of the reaction mixture should be able to diffuse in and out, the catalyst remains confined yet is able to perform translational and rotational motions, at least on a local scale.

It is obvious that zeolites, aluminum oxide and similar immobilizing systems used in heterogeneous catalysis can not be used for this purpose. However, synthetic polymers have

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distinct advantages for such applications. For example, it has been recognized for many decades that polymers are excellent choices as host matrices for guest–host systems designed for nonlinear optical applications, light-emitting diodes and information storage among other things.[5–7] Polymers frequently dissolve organic, metal organic, liquid crystalline low molar mass and oligomeric compounds up to high concentrations. This holds true not only for the molten but also for the solid glassy or partially crystalline state. Atactic polymers such as polystyrene or polymethylmethacrylate are solid glasses at room temperature. Yet due to local molecular motions that are present even in the solid glassy state—or the partially crystalline state for that matter—the guest molecules are able to perform rotational and translational motions within the glassy matrix and solvents or functional molecules are able to perform diffusional motions in such solid matrices.[7,8] All of these arguments imply that polymers might be used as carriers in homogeneous catalysis allowing for the preparation of products that contain only a trace amount of catalyst or that are even completely free of contamination. The polymer carrier may provide further advantages due to specific dynamic environments affecting the reactions, such as chiral environments.[9] In fact, the microencapsulation of polymer-based homogeneous catalysts based on polymers has been reported in the literature.[10,11] A typical approach involves the dispersion of the powdered catalyst in a polymer solution and the subsequent induction of a phase separation using methods such as a temperature drop. In this case, a powdered catalyst such as Sc, Os, Pd and Ru catalysts is covered by a thin polymer layer which can be hardened by solvent treatment. Polystyrene (PS) has been found to be the polymer material of choice. PS obviously provides specific interactions with such catalysts that reduce leaching.

Yet it seems that a molecular dispersion, rather than a microparticle dispersion, of the homogeneous catalyst within a particular carrier is closer to the concept of homogeneous catalysis and could therefore be potentially more effective. Furthermore, a molecular dispersion in combination with nanostructuring of the carrier should allow one to decrease the concentration of the catalyst significantly when compared with the microencapsulation approach. This will help to reduce the residual concentration of catalyst in the products even more. This paper is concerned with the preparation of carrier systems for homogeneous catalysis based on polymer fibers produced by electrospinning and considers scandium triflate-catalysed imino aldol and aza-Diels–Alder reactions as model reactions for homogeneous catalysis.

Results and Discussion

Choice of the catalyst and the model reactions: We selected commercially available scandium triflate (Sc(OTf)$_3$) as a catalyst which has been used in the microencapsulation approach reported in the literature.[10,11] An imino aldol and an aza-Diels–Alder reaction, which are displayed in Scheme 1,

were selected as test reactions. Polystyrene has previously been used in microencapsulation and for this reason we have selected polystyrene as polymer carrier for our investigations.
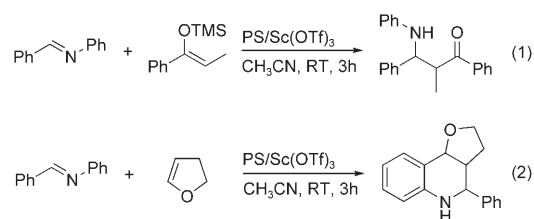
Scheme 1. Imino aldol and an aza-Diels–Alder model reactions.

Preparation of the fiber carrier: An important feature which will strongly affect the efficiency of the catalytic system is its architecture. It should be structured on a nanoscale since such a scale reduces the time required for the compounds in the reaction mixture to diffuse towards the catalysts contained within the carrier. Although polymer nanoparticles, thin films and porous membranes composed of polymers are possible architectures, it seems that non-woven fibers offer distinct advantages. Non-wovens composed of polymer fibers are used extensively for the filtering of gaseous and fluid media.[12–14] A large number of experimental and theoretical papers have dealt with the impact that internal specific surface, intrinsic pore sizes and the probability of fluid and gas particles within the non-woven fiber have on the nanofibers in the pores. The studies have found that the permeability of such non-wovens changes as a function of the orientation of the fiber in one-, two- or three-dimensional space, their total porosity and, most importantly, the fiber diameter.[15–17] These simulations as well as the corresponding experimental results clearly show that such non-wovens display features coming close to those of highly porous membrane structures of the type discussed above for heterogeneous catalysis with respect to pore size, internal surface and permeability. Provided that they are made from nanofibers, the advantage of the approach based on non-wovens is that they can be manufactured on a large scale from a large variety of polymers. Furthermore, the effect of aggregation of the fibers, a problem for the microencapsulated catalysts, which reduces the transport process, can be avoided by using suitable fiber textures such as random non-woven textures.

The technique of choice for nanofiber-based non-wovens is electrospinning.[12–14] For electrospinning of the polystyrene fibers we applied a strong electric field on the order of $10^3\ V\,cm^{-1}$ to the droplet of the polymer solution emerging from a cylindrical die. The electric charges accumulate on the surface of the droplet and cause it to become deformed along the field direction, even though the surface tension counteracts droplet evolution. In supercritical electric fields, the field strength overcomes the surface tension and a fluid jet emanates from the droplet tip. The jet is accelerated to-

wards the counter electrode. During this transport phase, the jet is subjected to strong electrically-driven circular bending motion which causes a strong elongation and thinning of the jet into a solvent evaporation until the solid fiber is finally deposited on the counter electrode. The fiber orientation can be controlled by suitable choices of the electrode configuration.

For the purpose of this study, electrospinning has additional advantages in that the catalytic species can be incorporated into the fibers during the electrospinning process. Moreover, porous fibers can be produced which enhance the surface area and the spatial arrangements of the fibers in space can be varied in order to control the permeability of such non-woven membranes.

Polystyrene was selected as the carrier for the model catalyst for the reasons described above. However, polystyrene is known to be one of the most difficult polymers as far as the electrospinning of fibers is concerned. To obtain non-woven fibers composed of polystyrene, we performed electrospinning using tetrahydrofuran, chloroform, dichloromethane and N,N-dimethylformamide solutions containing polystyrene in the concentration range of 5 to 20 wt %. The choice of the solvents is limited by the requirement that they should also be good solvents for scandium triflate. As shown in Figure 1a, spinning solutions containing lower concentrations of polystyrene result in fibers on which beads were superimposed. It turned out that THF is the best solvent for electrospinning. Figure 1b shows experimental results on the formation of non-wovens composed of polystyrene fibers with a thickness of approximately 1 μm.

The total porosity of such non-wovens is about 90 %. To immobilize $Sc(OTf)_3$ into the PS-fibers, we performed elec-

trospinning in tetrahydrofuran, chloroform, dichloromethane and N,N-dimethylformamide solutions containing both PS and the catalyst in a molecularly dispersed state and a polymer to catalyst ratio of 5 to 1. As before, THF is the best solvent for electrospinning of PS and $Sc(OTf)_3$. Fibers that are homogeneous in diameter were achieved, hereafter called catalytic system **A** (Figure 2). The diameter of the fibers amount to approximately 0.8 μm and the fibers are free of beads. We also measured the amount of $Sc(OTf)_3$ in the PS-fibers obtained by the electrospining process using atomic emission spectroscopy (AES). Starting with a polystyrene solution containing 16.5 wt % of $Sc(OTf)_3$ with respect to PS we found a $Sc(OTf)_3$ content of 14.8 wt % in the electrospun fibers, showing that most of the catalyst is indeed immobilized into the fiber during the electrospinning process.
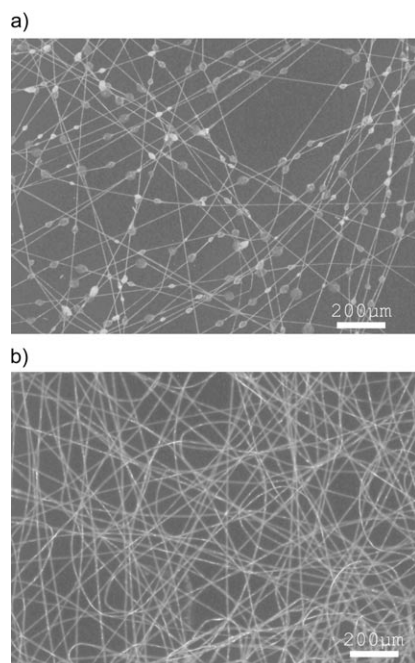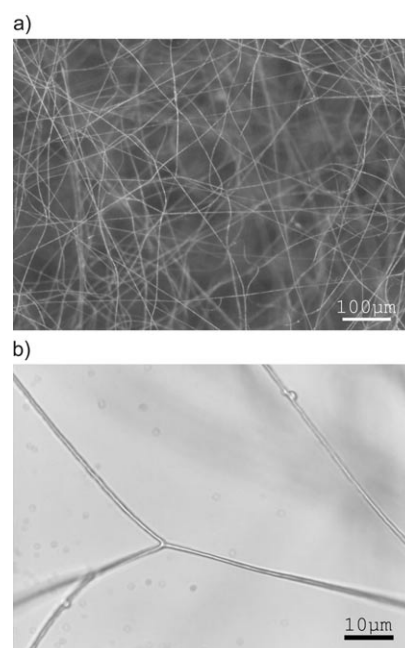

Figure 2. Fibers of PS obtained by electrospinning (catalyst **A**, optical microscopy): a) Non-woven web; b) individual fibers.

X-ray studies were performed on the fibers to obtain information on the state of dispersion of the catalyst within the fibers. The results are shown in Figure 3. The polystyrene fibers with and without the catalyst immobilized in them display only halos characteristic of amorphous polystyrene (i.e., the diagrams gave no indication of a phase separation and crystallization of the catalyst within the fiber). X-ray reflections characteristic of the pure $Sc(OTf)_3$ crystals are also shown in Figure 3.

Catalytic model reactions: The catalytic system **A** composed of the polystyrene fibers and the catalyst dispersed within them was first tested in the imino aldol reaction (Scheme 1, Equation (1)). To this end, the silyl enol ether (1.1 equiv), the imine (1.0 equiv) and system **A** (with 0.05 equiv of Sc-
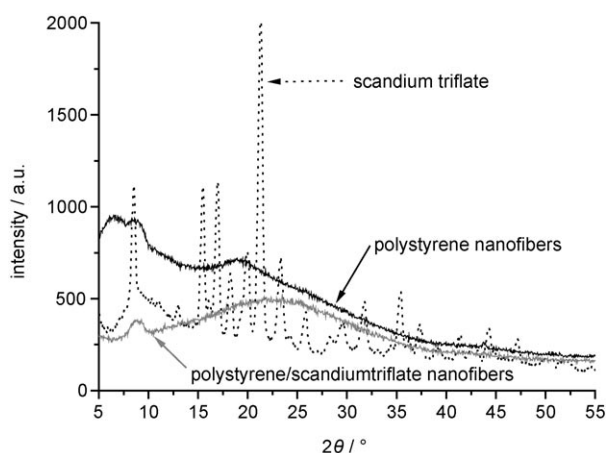

Figure 1. Fibers made via electrospinning from polystyrene/THF solutions a) with and b) without beads.

Figure 3. X-ray diagrams obtained for PS fibers, PS fibers with the catalyst immobilized and the pure catalyst scandium triflate.

(OTf)$_3$) were stirred at RT in CH$_3$CN for 2 h. Before each experiment, the catalyst was washed with CH$_3$CN for 30 min. The catalyst was recycled four times. The yield turned out to be a moderate 36% in run 1 and fell to 9% in run 4 as a result of leaching of the catalyst (Figure 4). More-
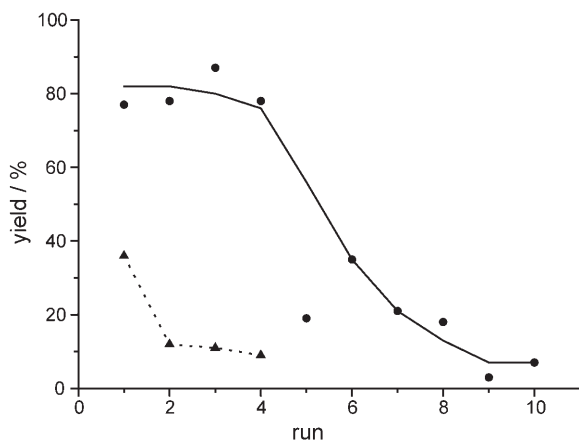

Figure 4. Dependence of the yield on the number of runs for the imino aldol reaction using catalysts **A** (▲) and **B** (●). Yields were determined by ^{1}H NMR spectroscopy. Diastereoisomer ratio 1.1:1.

over, the mechanical stability of catalyst **A** was not satisfactory.

**Modification of the non-woven carrier system**: In light of the apparent leaching processes, we decided to coat the fibers carrying the catalyst with a thin polymer film to obtain core shell functional fibers.[18,19] The approach consisted in depositing this shell layer via chemical vapor deposition (CVD) starting from [2.2]paracyclophane in a first set of experiments as precursor following the approach reported by Gorham.[20] In

this case, poly-p-xylylene (PPX) is deposited at 30°C (Scheme 2). The layer thickness depends on the deposition time. PPX is known to be partially crystalline and, therefore, resistant to most common solvents.

Figure 5 displays PS-fibers (diameter 0.8 μm) covered with a 0.2 (catalytic system **B**) and 0.4 μm thick PPX layer (catalytic system **C**). To modify the permeation of the catalyst through the shell layer even further, we replaced the [2.2]paracyclophane by [2.2]para(chlorocyclophane) in a second set of experiments. It is known from the literature that the poly-p-chloroxylylene (PPX-C) films are characterized by lower permeation coefficients for small molecules when compared with the unmodified PPX. In this case, fibers with a diameter of 0.8 μm were covered by a thin PPX-C film having a thickness of 0.5 μm (catalyst **D**). To the best of our knowledge, this is the first report on the immobilization of a catalyst in core/shell fibers.

Catalytic model reactions with core/shell fibers: The catalyst efficiency is found to increase sharply as one moves from the parent system **A** to the core/shell catalytic system **B** (Figure 4). Thus, the yield for the imino aldol reaction increased from 36 to 77% in run 1. Moreover, the yield remained high for the first four runs (Figure 4). Afterwards, a decrease in the catalyst efficiency was observed, probably due to leaching (see below). Importantly the catalyst activity stabilized to approximately 10% conversion under the applied conditions after initial leaching. Additionally, the physical stability of the catalyst increased such that no change in the morphology of the hybrid catalyst was observed after several runs.

Next, the aza-Diels–Alder reaction using catalyst **C** was studied. The results are displayed in Figure 6. The yield amounts to 100% in the first two runs and is thus significantly higher than the 80% reported in the literature for the microencapsulated catalysts. However, less than 5 mol% of Sc(OTf)$_3$ was used in our system (3 h reaction time) compared with the 50 mol% Sc(OTf)$_3$ used for the microencapsulated analogue (4 h reaction time).[10] The yield decays after the second run down to and then stabilizes at approximately 20%. No further decrease of activity was observed after run 7. We were pleased to note that the replacement of the PPX shell polymer by the PPX-C shell polymer led to
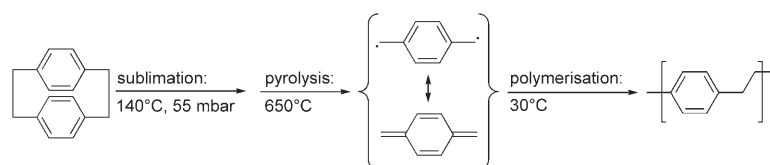
Scheme 2. Scheme of the PPX-deposition on electrospun fibers.

further improvement of the results. The yield stays at 100% using catalyst **D** for up to five runs and then decays for a higher number of runs. Thus, leaching can be slowed down upon switching to the chlorinated shell. Importantly, as with
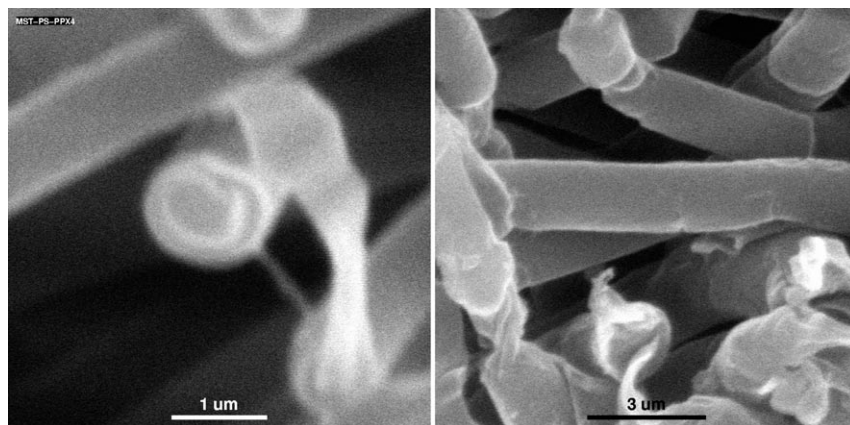
Figure 5. Core/shell fibers with polystyrene and the catalyst scandium triflate as core material (800 nm) and PPX as shell material (SEM images). Shell-thickness: 200 nm, catalyst **B** (left); shell-thickness: 400 nm, catalyst **C** (right).

initial phase of the reaction (up to 75 minutes) the immobilized catalyst is even more active compared with the reaction conducted using non-immobilized scandium triflate. However, a slightly higher yield is obtained for the reaction conducted in homogeneous solution. Importantly, these kinetic experiments clearly show that our new immobilization approach delivers reusable catalysts with catalytic activities comparable or even slightly higher to the activities obtained with the corresponding homogeneous systems.

the other immobilized catalysts discussed above, catalyst activity stabilized at a value of approximately 10–20% of the initial activity after initial leaching.
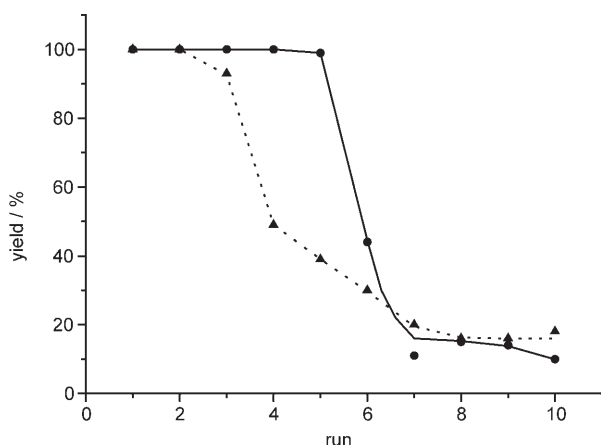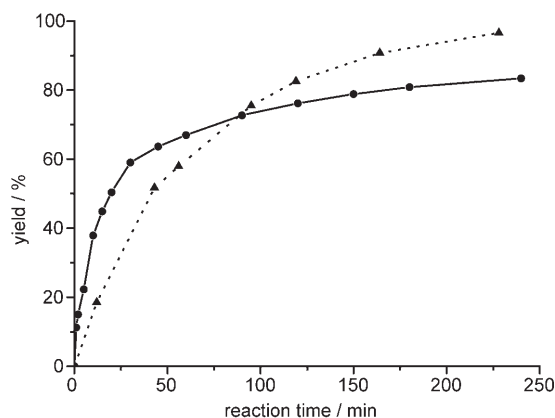

Figure 6. Dependence of the yield on the number runs for the aza-Diels–Alder reaction using catalysts **C** (▲) and **D** (●). Yields were determined by ^{1}H NMR spectroscopy. The product was formed as a 55:45 mixture of diastereoisomers.

Figure 7. Kinetics of the aza-Diels–Alder reaction catalyzed by scandium triflate immobilized in fibers of type **D** (●: PS diameter = 0.8 μm, PPX-C thickness = 0.7 μm) and in homogeneous solution (▲). Sc(OTf)$_3$ loading was 0.07 mol% in both experiments.

The Figure 7 displays the dependence of the yield of the aza-Diels–Alder reaction as a function of time using a catalyst of type **D** (PS-diameter = 0.8 μm, PPX-C thickness = 0.7 μm). Prior to the reaction the catalyst system was washed with acetonitrile for 16 h (to remove the weakly adsorbed Sc(OTf)$_3$ which is extracted in the first few runs in the experiments, see leaching studies below). AES investigations revealed a Sc(OTf)$_3$ content of 8.2 wt% after this extensive washing procedure. For the kinetic experiment using this fiber, the Sc(OTf)$_3$ concentration was set to 0.07 mol%. A comparison with the corresponding results obtained for the experiment run with a homogeneous solution of the catalyst containing 0.07 mol% of Sc(OTf)$_3$ reveals that in the

To investigate leaching, AES investigations were performed and the results are shown in Figure 8. These investigations revealed that a major portion of the catalyst was removed within the pre-washing process and the first run which was followed by rinsing. Importantly, the small amount of Sc(OTf)$_3$ remaining in the core/shell nanofiber after the first few cycles is still able to catalyze the reaction. Considering the low catalyst loading after initial leaching, the system shows an amazing catalytic activity. This is further supported by the kinetic experiments depicted in Figure 7. The high activity observed in the first few runs can be understood by catalysis occurring inside the fibers as well as in solution by extracted Sc(OTf)$_3$. Moreover, the lower catalyst activity of catalyst **A** compared with the core/shell type system **B** (see Figure 4) can be explained by the extraction of large amounts of Sc(OTf)$_3$ in the non-coated system **A** during the pre-washing process.
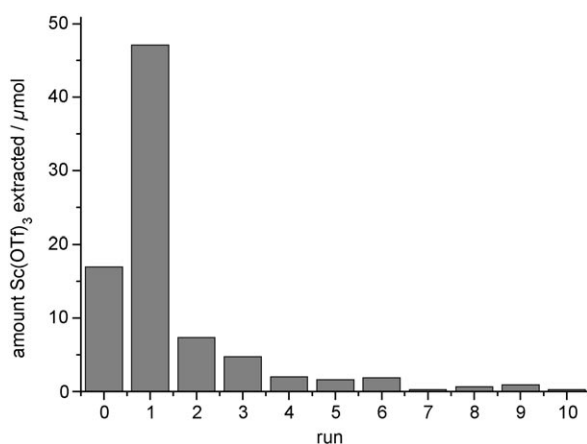
Figure 8. Results of atomic emission spectroscopy on the leaching of the catalyst from the core/shell nanofiber **D** prepared using 84 µmol Sc-(OTf)$_3$. Run 0 designates extracted Sc(OTf)$_3$ during the pre-washing process (30 min). For each run, the total amount Sc(OTf)$_3$ extracted during the reaction (3 h) and during the rinsing process (30 min) was added.

Conclusion

In summary, homogeneous catalysts can be immobilized within core/shell polymer fibers without loss of their activity. It was observed that catalyst activity is not decreased upon immobilizing. Still, one problem is the tendency for leaching to occur during the first few runs. After initial leaching, however, the catalyst activity remained constant at a value of about 10–20 % of the initial catalyst activity. Importantly the results reported above have shown that leaching can be strongly influenced by variation of the shell material. We also intend to vary the core material in order to reduce leaching. It is obvious that a higher concentration of the catalyst inside the core/shell fiber will ensure a higher catalyst activity. In any case, our results strongly suggest that the immobilization of homogeneous catalysts in polymer fibers is a highly promising approach which can easily be applied and used in flow systems or in microreaction set-ups.

Experimental Section

Electrospinning of PS/Sc(OTf)$_3$ fibers: Polystyrene (1.000 g) and Sc-(OTf)$_3$ (0.200 g) were dissolved in THF (7.64 mL). The solution, stored within a reservoir, was pumped through a metal capillary using a peristaltic pump connected with a voltage supply. The circular orifice of the capillary had a diameter of 0.3 mm. A circular shaped counter electrode with a diameter of 18 cm was located below the reservoir resulting in a vertical arrangement of the electrodes. Fibers were collected on aluminum foil. The distance between the tip of the capillary and the counter electrode was typically on the order of 15 cm and the applied voltage was 30 kV.

Coating of fibers by chemical vapor deposition (CVD): PPX and PPX-C deposition from the gas phase was accomplished by vapor phase pyrolysis of the starting material [2.2]paracyclophane and [2.2]dichloroparacyclophane, respectively. The subsequent CVD of the corresponding pyrolysis product yielded 1,4-quinodimethane and 1,4-quinochlorodimethane, respectively.[20]

Preparation of the reaction component *N*-benzylideneaniline: Benzene (11 mL), aniline (2.5 mL, 28 mmol), benzaldehyde (2.8 mL, 28 mmol), NaHCO$_3$ (11.5 g, 138 mmol) and molecular sieve 3 Å were placed in a Schlenk tube. The mixture was heated under reflux for 19 h. The suspension was filtered and washed with water (3x30 mL), 2 M NaOH solution (1×30 mL), saturated NaHCO$_3$ solution (1×30 mL) and saturated NaCl solution (1×30 mL). The organic phase was concentrated under reduced pressure to give the pure product (4.67 g, 92 %).[21]

Preparation of the reaction component (*Z*)-1-phenyl-1-trimethylsiloxy-propene: THF (170 mL) and diisopropylamine (7.0 mL, 50 mmol) were placed in a Schlenk tube. The mixture was cooled to 0 °C. A solution of BuLi in hexane (29.8 mL, 1.6 M, 50 mmol BuLi) was added and then stirred for 45 min. The mixture was cooled to −70 °C and propiophenone (6.6 mL, 50 mmol) was added dropwise. After stirring for 30 min, chlorotrimethylsilane (6.3 mL, 50 mmol) was added. The solution was stirred at room temperature for 1 h. After adding triethylamine (57 mL), the solution was poured into pentane (1 L). The white precipitate that formed was filtrated and washed with pentane. The organic phase was extracted with water (3×400 mL), dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel to give (*Z*)-1-phenyl-1-trimethylsiloxypropene (7.75 g, 75 %). The physical data are in agreement with those reported in the literature.[22]

Imino aldol reaction: Immobilized Sc(OTf)$_3$ (fiber prepared using 203 µmol Sc(OTf)$_3$) was washed with CH$_3$CN for 30 min and subsequently placed in a Schlenk tube containing CH$_3$CN (30 mL). *N*-Benzylideneaniline (4.0 mmol) and (*Z*)-1-phenyl-1-trimethylsiloxypropene (4.4 mmol) were then added. The mixture was stirred for 2 h. The catalyst was removed followed by evaporation of the solvent. Yields were determined by ^{1}H NMR spectroscopy. The recovered immobilized catalyst was washed with CH$_3$CN for 30 min and used for the next run. The physical data are in agreement with those reported in the literature.[23]

Aza-Diels–Alder reaction: Immobilized Sc(OTf)$_3$ (fiber prepared using 84 µmol Sc(OTf)$_3$) was washed with CH$_3$CN for 30 min and subsequently placed in a Schlenk tube containing CH$_3$CN (24 mL). *N*-Benzylideneaniline (1.7 mmol) and 2,3-dihydrofuran (2.5 mmol) were added. The mixture was stirred for 3 h. The catalyst was removed followed by evaporation of the solvent. Yields were determined by ^{1}H NMR spectroscopy. The recovered immobilized catalyst was washed with CH$_3$CN for 30 min and used for the next run. The physical data are in agreement with those reported in the literature.[24]

Characterization: The X-ray analysis was performed with a Siemens D 5000 wide-angle goniometer. Scanning electron microscopy was performed with a JEOL CamScan 4 microscope using acceleration voltages between 15 and 20 kV. Atomic Emission Spectra (AES) were measured using an argon-plasma and a SpectroFlame-EOP detector (Spectro Analytical Instruments GmbH).

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