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PAPER

Pore size control and organocatalytic properties of nanostructured silica hybrid materials containing amino and ammonium groups[†]

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Periodic mesoporous organosilicas containing amine and ammonium substructures were synthesized *via* soft templating approaches using anionic surfactants. Pore size control was achieved either using anionic surfactants containing alkyl groups of variable chain lengths or by addition of swelling agents such as mesitylene (1,3,5-trimethylbenzene, TMB) to the hydrolysis–polycondensation mixture. The addition of mesitylene allows to increase the pore size in the materials from 2 to 6 nm. The materials appear as versatile and recyclable heterogeneous organocatalysts in Knoevenagel and Henry reactions and in the formation of monoglycerides by ring opening reaction of glycidol. This study highlights the huge potential of silica hybrid materials containing ionic substructures (*i-silica*) materials in heterogeneous catalysis.

1. Introduction

Soft templating approaches are largely used for the generation of nanostructured metal oxides and in particular in the field of the synthesis of mesoporous nanostructured silica materials.¹ Conventional soft templating routes to nanostructured silica involve hydrolysis–polycondensation procedures of molecular silica network formers such as tetraethyl-*ortho*-silicate (TEOS) in the presence of cationic² or neutral structure directing agents.^{3,4} These reactions give rise to the formation of mesoporous and nanostructured silica phases which are characterized by high surface areas (up to 1500 m² g⁻¹), narrow pore size distributions and regular pore arrangements on a mesoscopic length scale.⁵

Pore size control in soft templating approaches was intensively studied. The simplest way to tune the pore size in micelle templated silica consists of using surfactants containing alkyl chains with variable chain length. However, this strategy afforded pore size control over a rather small range on a supermicroscopic or small mesoscopic length scale. For example, increasing the alkyl chain lengths of cationic trimethyl-alkyl ammonium templates from C_8 to C_{16} increases the BJH pore diameters of the resulting mesoporous MCM-41 molecular sieve from 1.6 to 3.2 nm.⁶ Another strategy to tune the pore size in template directed hydrolysis–polycondensation procedures consists of the addition of organic solvent to the reaction mixtures. The addition of swellers such as mesitylene (1,3,5-trimethylbenzene, TMB) increases the size of the micelles in the hydrolysis–polycondensation mixtures. This strategy allows to control the pore size in mesoporous materials over a larger range. For MCM-41 type materials, obtained in the presence of cationic surfactants,⁷ pore diameters up to 12 nm were achieved. For SBA-15 type materials, obtained with non-ionic structure directing agents such as Pluronic© P123, average pore diameters as large as 30 nm were observed.³

Periodic mesoporous organosilicas (PMOs)8-10 recently emerged as a new class of versatile functional materials. PMOs are characterized by a homogeneous distribution of organic groups throughout the whole hybrid material on a molecular level and display regular architectures on a mesoscopic length scale.¹¹⁻¹³ PMO type materials are typically synthesized by template directed hydrolysis-polycondensation of bridged bistrialkoxysilylated precursor molecules [(R'O)₃Si-R-Si(OR')₃].¹⁴ This approach gives rise to the formation of a whole set of functional organic-inorganic hybrid materials containing e.g. chiral fragments,¹⁵⁻¹⁹ π -conjugated segments^{20,21} or chelating entities.²² These materials found wide applications in catalvsis,^{23,24} sorption²⁵ and optics.^{20,21,26} Bifunctional PMOs synthesized from two or more organic precursor molecules have also been reported. The incorporation of multiple bridging groups allows to fine tune the surface properties of PMOs and to achieve desired functionality and selectivity.²⁷⁻³³ Pore size control in PMO type materials can be achieved following similar strategies as reported for mesoporous silicas.³⁴ For example, the addition

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[†] Electronic supplementary information (ESI) available: SEM-images of materials A16A18, 1/5, 1/10; nitrogen sorption isotherms of materials A12, A14, 1/5, 1/20, 1/40; plot of the pore-pore distance in the materials vs. molar TMB/surfactant ratio. See DOI: 10.1039/c1jm10422e

of TMB to hydrolysis–polycondensation mixtures allowed to expand the pore size diameters in ethane and ethenylene bridged PMO type materials up to 20 nm.^{35,36}

The use of ionic precursors in template directed hydrolysispolycondensation procedures gives rise to the formation of PMO-type materials bearing ionic groups (i-silica). These materials have high potential in catalysis,³⁷⁻³⁹ separation⁴⁰ and electro-optics.^{41,42} We particularly focus on the synthesis of materials with original architectures on a mesoscopic length scale. We especially addressed the question of whether the ionic nature of the precursors influences the architecture of the resulting *i-silicas* formed in template directed hydrolysis-polycondensation procedures and may result in the formation of original materials, which are inaccessible from conventional neutral precursors. In this field, we recently reported nanostructured silica hybrid materials bearing imidazolium43,44 and ammonium halides,45 but also surface functionalized silicas containing guanidinium sulfonimide ion pairs.⁴⁶ We observed that highly structured and porous silica hybrid materials are formed from silvlated cationic precursors via soft templating approaches using long chain substituted sulfates as structure directing agents. This study points to an unusual mechanism for the generation of nanostructured silica hybrid materials, as anionic surfactants are usually inappropriate structure directing agents for the formation of nanostructured silica or silica hybrid materials. We attributed the formation of structured i-silica phases to ionic interactions between the anionic head groups of the sulfate surfactants and 'organo-cationic' substructures of the silvlated hybrid precursors (Scheme 1).

In the field of the synthesis of functional PMO type materials, our finding is of particular interest as it represents the first example for the formation of nanostructured silica hybrid materials by interactions involving the organic bridging unit of silylated precursors. These interactions are specific for positively charged precursors and allow to access original nanostructured silica hybrid materials which are not accessible following standard procedures.^{44,45} In this context, Yokoi and Che already reported the so-called anionic surfactant templated mesoporous silica (AMS),^{47–51} synthesized by co-condensation reactions of silylated ammonium precursors with silica network formers (TEOS). In this way, highly structured silica^{48,49} and chiral mesoporous silica^{50,51} were obtained.

Here, we focused on two different aspects concerning the processing of cationic silylated precursors and the synthesis of nanostructured silica hybrid materials containing amine and ammonium groups obtained from the trisilylated amino precursor **1** (Scheme 2). Firstly, we studied the morphologies of the materials formed *via* soft-templating routes using anionic



Scheme 1 Sol-gel processing of cationic precursors using anionic structure directing agents (from ref. 45).



Scheme 2 Tris(3-(trimethoxysilyl)propyl)amine precursor 1.

surfactants. The synthesis of nanostructured *i-silica* in the presence of sodium cetyl stearyl sulfate systematically afforded materials displaying pore diameters in the supermicroscopic/ mesoscopic length scale (20–22 Å). Here, we report strategies to tune the pore size in these materials. Secondly, we monitored the catalytic potential of these original materials in various organocatalytic reactions: Knoevenagel condensation, Henry reactions and the monoglyceride synthesis by ring opening of glycidol.

2. Experimental

2.1 General details

The precursor tris(3-(trimethoxysilyl)propyl)amine **1** was synthesized following a previously described protocol.⁴⁵ The anionic sulfate surfactants sodium dodecyl sulfate (SDS), sodium tetradecylsulphate (STS) and sodium cetyl stearyl sulfate (60% sodium hexadecylsulfate/40% sodium octadecyl-sulfate) were purchased from ABCR. ¹H and ¹³C spectra in solution were recorded on Bruker AC 250 or Bruker Avance 400 spectrometers at room temperature. Deuterated chloroform was used as solvent for liquid NMR experiments and chemical shifts are reported as δ values in parts per million relative to tetramethylsilane.

Nitrogen sorption isotherms were obtained at 77 K with a Micromeritics ASAP 2020 apparatus. Prior to measurement, the samples were degassed for 18 hours at 100 °C. The surface areas (S_{BET}) were determined from BET treatment in appropriate p/p_0 ranges and assuming a surface coverage of nitrogen molecule estimated to be 13.5 Å². Pore size distributions were calculated from the adsorption branch of the isotherms using the BJH method. The pore width was estimated at the maximum of the pore size distribution. XRD experiments were carried out with a Xpert-Pro (PanAnalytical) diffractometer equipped with a fast X'celerator detector using Cu-K α radiation.

2.2 Materials synthesis

Sodium cetyl stearyl sulfate (266 mg, 0.77 mmol) was dissolved under stirring at 60 °C in a solution prepared from deionized water (17.9 g) and 2 ml of 1 M hydrochloric acid. To this solution, variable quantities x mmol of mesitylene were added (x =0.77, 3.85, 7.7, 15.4, 30.8, 61.6).

After the mixture has been stirred for 1 h, a solution of the amine precursor 1 (1 mmol, 0.5 g), dissolved in a mixture containing 1 g of water and 0.5 g of ethanol, was rapidly added to the surfactant solution. The resulting mixture was vigorously stirred at 60 °C for 20 min. After this time, the mixture was heated at 70 °C under static condition for 72 h. The resulting solid products were recovered by filtration and dried under air at 70 °C for 15 h. The surfactant was removed by washing 0.5 g of the solid with a solution of 100 ml ethanol/5 ml conc. hydrochloric acid or

100 ml ethanol/5 ml NH_4Cl and NH_3 (25%) to give silica hybrid materials containing ammonium or amine groups after drying.

2.3 Organocatalytic tests

Knoevenagel condensation. Benzaldehyde (531 mg/5 mmol) was dissolved in 5 ml of the corresponding solvent. To this solution were added 30 mg of the catalyst **A16A18** and malononitrile (330 mg/5 mmol). The resulting reaction mixture was stirred at 50 °C for 30 min. After this time, the catalyst was filtered and the filtrate was concentrated. The product was analysed by ¹H NMR. The catalyst was washed with the corresponding solvent, dried and re-used.

Henry reactions. The reactions were carried out in the presence of different *p*-substituted benzaldehydes solved in nitroethane by using either the material A16A18 or A16A18-p as catalysts. In a typical procedure, to a solution of the aldehyde (1 equiv.) in nitroethane (20 equiv.) was added the catalyst (0.15 equiv., 5.88 mmol organic precursorper gram material, obtained from TGA). The same molar ratio was kept when ammonium salts were used as catalysts. The mixture was stirred, under air, at room temperature for the appropriate time. After that, the material was filtered off, washed with ethanol (3 × 10 ml) and dried at 75–80 °C overnight (18 h) for its use in a posterior cycle. Conversions and *syn*: *anti* ratios were assessed by ¹H-NMR analysis of aliquots of the crude reaction mixture, from which the nitroethane had been previously evaporated under vacuum.

Monoglyceride synthesis by ring opening of glycidol. Lauric acid (500 mg, 2.5 mmol) is added to a suspension of 200 mg of the material **A16A18** or **A16A18-p** in toluene (10 ml). Glycidol (200 mg, 2.6 mmol) was added and the reaction mixture was heated to reflux during 3 h under vigorous stirring. After cooling, the solid catalyst was separated by filtration and dried. The filtrate was concentrated yielding a solid product which was recrystallized from hexane and finally analyzed by ¹H NMR spectroscopy.

3. Results and discussion

In a first series of experiments, we used sulfate surfactants bearing alkyl chains of variable length as structure directing agents. Hydrolysis-polycondensation reactions were performed from the amine precursor 1, water, 1 M hydrochloric acid and anionic surfactant [sodium dodecyl sulfate (SDS), sodium tetradecyl sulfate (STS) or sodium cetyl stearyl sulfate (SHS)] in the molar composition 1/1111/2/0.77. The materials A12, A14 and A16A18 containing amine groups were obtained after surfactant elimination in basic media (ethanol-ammonia). A related protonated material A16A18-p was synthesized under similar reaction conditions except the final washing step, carried out under acidic conditions (ethanol-hydrochloric acid). The characterization of these materials by nitrogen sorption showed that a minimum length of the alkyl chain in the anionic surfactant is necessary for the formation of porous phases. Strongly increasing specific surface areas can be seen in the order A12-A14-A16A18 (Table 1). Hydrolysis-polycondensation of precursor 1 under the above mentioned conditions in the

Table 1 Surface properties of the materials

Material	Surfactant	$S_{ m BET}/m^2~{ m g}^{-1}$	Average pore diameter ^a /Å	Mesopore volume ^c / cm ³ g ⁻¹
A12	SDS	210		0.15
A14	STS	$790^{\check{b}}$	_	0.32
A16A18	SHS	1120^{b}	<20	0.58
A16A18-p	SHS	970^{b}	<20	0.45
Material 1/1	SHS	1180^{b}	~ 20	0.67
Material 1/5	SHS	966	42	0.99
Material 1/10	SHS	915	44	0.95
Material 1/20	SHS	831	54	0.90
Material 1/40	SHS	795	58	0.96
Material 1/80	SHS	844	60	1.04

^{*a*} Estimated at the maximum of the BJH pore size distribution obtained from the adsorption branch of the isotherm. ^{*b*} Determined at p/p_0 values >0.05 and <0.15. ^{*c*} Determined from adsorption isotherm from the N₂-quantity at the end of the capillary condensation.

presence of sodium cetyl stearyl sulfate yielded the highly structured supermicroporous material A16A18 showing a specific surface area S_{BET} of 1120 m² g⁻¹ and an average pore diameter of approx. 20 Å.⁴⁵ The related materials A16A18-p showed similar characteristics but slightly reduced specific surface area and pore volume. In a second set of experiments, we studied hydrolysis-polycondensation reactions of precursor 1 in the presence of defined amounts of 1,3,5-trimethylbenzene (TMB). These reactions were carried out with sodium cetyl stearyl sulfate and 0.77, 3.85, 7.7, 15.4, 30.8 and 61.6 eq. TMB in the reaction mixtures with respect to precursor 1, giving rise to the materials 1/1, 1/5, 1/10, 1/20, 1/40 and 1/80. Nitrogen sorption experiments with these materials indicated a strong influence of the TMB amount in the reaction mixture on the morphology of the formed materials. The principal trends can be seen from the shape of the nitrogen sorption isotherms of the materials A16A18, 1/1, 1/10 and 1/80 shown in Fig. 1. The results are summarized in Table 1. The comparison of the isotherms shows slightly decreasing specific surface areas for increasing TMB amounts in the reaction mixtures as indicated by lower nitrogen uptake at low pressures ($p/p_0 < 0.3$) of materials 1/10 and 1/80 compared to the materials A16A18 and 1/1. Furthermore, the



Fig. 1 Nitrogen adsorption–desorption isotherms of materials **A16A18**, **1/1**, **1/10** and **1/80**. The isotherms of the other materials are omitted for clarity and given in the ESI† (Fig. S1).

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 N_2 -uptake in the mesopore range progressively shifts to higher pressures indicating increasing pore diameters in the materials for increasing amounts of TMB.

These results are reflected by the BJH pore size distribution curves of the materials, showing progressively increasing average pore diameters for increasing amounts of added TMB in the reaction mixtures. The materials show a progressive pore size increase from approx. 20 Å for materials A16A18, A16A18-p and 1/1 up to 60 Å for material 1/80 (Fig. 2). The pore size distribution becomes larger when high amounts of TMB were added to the hydrolysis–polycondensation mixture. Finally, the mesopore volume of the materials obtained in the presence of TMB is relatively constant and considerably higher than the value observed for the supermicroporous A16A18 material. It should be noted that further increase of the TMB quantity did not result in further expansion of the pores and only gave less structured materials with reduced mesopore volumes.

The results of X-ray diffraction measurements (Table 2) also reflect the morphological changes in the materials. The (100) reflection progressively shifts from 2θ angles of 2.9° (material **A12**) to 0.850° (material **1/40**) corresponding to pore–pore distances of 30 Å in the material **A12** to more than 100 Å in the case of the material **1/40**. The plot of the pore–pore distance, obtained from the XRD measurements, *vs.* the molar TMB/ surfactant ratio in the hydrolysis–condensation mixture shows an asymptotic shape with a maximum value of approx. 140 Å (ESI[†], Fig. S2). However, both the use of short chain surfactants and the addition of TMB to the hydrolysis–polycondensation mixture result in the formation of materials with lower structural regularity and the generation of worm-like architectures. The formation of materials with lower regularity on a mesoscopic



Fig. 2 BJH pore size distribution of selected materials, obtained from the adsorption branch of the isotherm.

Table 2 Results from XRD measurements

Material	$d_{100}/2\theta$ value	$d_{100}/\text{\AA}$	Pore-pore distance/Å
A12	2.9	30	35
A14	2.5	35	40
A16A18	2.377	37	43
Material 1/5	1.224	72	83.3
Material 1/10	1.123	78	90.8
Material 1/20	0.952	93	107
Material 1/40	0.850	104	120



Fig. 3 Small angle X-ray diffractograms of materials A12, A16A18 and 1/5, 1/10 and 1/20, formed in the presence of various amounts of TMB.

scale was already suggested by a broader pore size distribution (*vide supra*) and can be seen here by the broad shape of the (100) reflections and the absence of reflections of higher order in the materials A12, A14, 1/5, 1/10, 1/20 and 1/40 (Fig. 3). The negative effect of TMB addition on long-range ordering in the resulting materials has already been reported in the case of ethenylene-bridged PMOs.³⁵

Characterization of the materials by scanning electron microscopy (SEM) showed that all materials have very similar morphology and consist of agglomerated particles of 100–200 nm in diameter (Fig. 4).

4. Organocatalysis

PMO type materials found widespread applications in heterogeneous catalysis.²³ Here, we focus in particular on metal-free catalytic transformations. We tested the amine containing PMO material **A16A18** as heterogeneous organocatalyst in three different reactions: Knoevenagel condensations, Henry reactions and the formation of monoglycerides by ring opening of glycidol.

Knoevenagel condensations

Knoevenagel reactions are often applied to monitor the catalytic potential of amine functionalized silica.^{52–57} In a preliminary study, we screened the catalytic properties of the amine functionalized PMO material **A16A18** as a heterogeneous catalyst for Knoevenagel condensations of benzaldehyde and malononitrile (Scheme 3), affording benzylidenemalononitrile as the sole product. The results are summarized in Table 3.



Fig. 4 SEM-image of material 1/5.

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Scheme 3 Knoevenagel condensation.

 Table 3
 Conversions in Knoevenagel reactions of benzaldehyde and malononitrile using the material A16A18 as heterogeneous catalyst

Entry	Solvent	Conversion (%)	Entry	Solvent	Conversion (%)
1^{a} 2^{b} 3	EtOH EtOH MeOH EtOH	0 0 100 97	7 8 9	CHCl ₃ CH ₂ Cl ₂ ^{c} EtOH, 2 nd run EtOH, 3 rd run	76 61 96
5 6	THF CH ₃ CN	79 66	10 11 12	EtOH, 5 th run EtOH, 5 th run	93 94 95

^{*a*} Reaction without catalyst. ^{*b*} Reaction carried out in the presence of SBA-15 type mesoporous silica. ^{*c*} Reaction carried out under reflux of CH₂Cl₂.

As already reported for other heterogeneous base catalyst systems, polar protic solvents such as methanol or ethanol gave the highest conversion rates in Knoevenagel reactions (Table 1, entry 3,4) whereas polar aprotic solvents gave lower conversions. Recycling experiments showed unchanged catalytic activities of material **A16A18** in up to 5 runs (entries 9–12). The results of this preliminary study highlight the potential of these new amine functionalized PMO materials in heterogeneous catalysis and prompted us to study two other more ambitious test reactions.

Henry reactions

The Henry Reaction is a base-catalyzed C–C bond-forming reaction between nitroalkanes and aldehydes or ketones (Scheme 4) to yield β -nitroalcohols which are valuable synthetic building blocks for the synthesis of pharmacologically important building blocks.⁵⁸ Amine functionalized silicas are efficient promoters of Henry reactions as recently shown by Asefa *et al.* and Wang and Shantz.^{59,60} Here, we studied in particular the Henry reaction of benzaldehyde with nitroethane (Scheme 4, R = CH₃).^{61,62} The results of these experiments are summarized in Table 4.

Preliminary experiments showed that neither mesoporous SBA-15 type silica nor ammonium salts efficiently promote Henry reactions of *p*-nitrobenzaldehyde and nitroethane. Only the use of methyl triethylammonium chloride showed low conversion and led to the formation of the desired product after long reaction time and heating (entry 3). In contrast, the reaction is efficiently catalyzed by tertiary amines. The reaction in the presence of triethylamine yields the corresponding β -



Scheme 4 Themy reaction

Table 4 Conversions in Henry reactions of *p*-nitrobenzaldehyde and nitroethane using the materials **A16A18** and **A16A18-p** as heterogeneous catalysts

Entry	Catalyst	Time/h	Conversion (%)	Syn/anti ratio
1	None	48	0	
2	SBA-15	4	0	
3	MeN ⁺ Et ₃ Cl ^{-a}	92	18	43:57
4	HN ⁺ Et ₃ Cl ⁻	72	0	
5	NEt ₃ 61	1	85	57:43
6	A16A18	4	97%	56:44
7	A16A18 2nd run	4	67%	58:42
8	A16A18 3rd run	4	>99%	47:53
9	A16A18 4th run	4	>99%	48:52
10	A16A18 5th run	4	>99%	45:55
11	A16A18-p	4	47	40:60
12	A16A18-p 2 nd run	4	34	40:60
13	A16A18 ^b	4	77	66:34
14	A16A18 ^c	4	33	52:48
	tion tommomotumo	45 °C	^b Departien	miad out with

^{*a*} Reaction temperature: 45 °C. ^{*p*} Reaction carried out with p-bromobenzaldehyde. ^{*c*} Reaction carried out with p-anisaldehyde.

nitroalcohol in 85% yield with a syn/anti ratio of 57:43.61 Following these results, we tested out the amine containing material A16A18 as a heterogeneous catalyst for Henry reactions. This material showed high catalytic activity in Henry reactions and led to the corresponding β -nitroalcohol in 97% yield after 4 h in a first reaction cycle (entry 6). Interestingly, the obtained product showed a syn/anti ratio of 56 : 44 which is in nice agreement with the result obtained with free triethylamine (entry 5). Following these results, we tested the recycling of the heterogeneous A16A18 catalyst. We observed a decrease of the catalytic activity in the second reaction cycle, but a new increase of the conversion starting from the 3rd cycle, giving the reaction product in nearly quantitative yield in the 3rd, 4th and 5th cycle. The regioselectivity observed in the recycling experiments displays another tendency. Whereas the syn/anti ratio in the first reaction cycle (56:44, entry 6) is in nice agreement with the result obtained with triethylamine (57:43, entry 5), this ratio progressively inverts in the following cycles, and finally shows a value of 45 : 55 in the 5th cycle (entry 10). These results may indicate that the catalytic site undergoes some changes during the cycles.

We therefore studied the protonated material A16A18-p as a heterogeneous catalyst for the Henry reaction. This material was obtained in a similar way as the material A16A18, but the template elimination of the parent material was carried out under acidic conditions. This material therefore contains protonated trialkylammonium substructures. The evaluation of the catalytic properties of the material A16A18-p showed reduced catalytic activity with conversions of 47 and 34% in the first and second reaction cycle, respectively. In both reactions, the formed β -nitroalcohol showed an identical syn/anti ratio of 40 : 60 (entries 11/12).

These whole results suggest that the changes of the catalytic activity and diastereoselecitvity observed in the recycling experiments of material A16A18 may be due to a partial protonation of the immobilized amine sites. It has to be mentioned that the recycled material A16A18 shows a higher catalytic activity compared to triethylamine on the one side, but also compared to

the freshly synthesized materials A16A18 and A16A18-p. These results suggest some synergistic effects in the materials involving both immobilized amine and ammonium substructures and the silica hybrid network. These synergistic effects may be responsible for the enhanced catalytic activity of re-used materials together with the inversion of the regioselectivity we observed in the recycling experiments of material A16A18.

Finally, it has to be mentioned that the conditions of the Henry reaction affected neither the chemical integrity of the immobilized amine substructures nor the surface properties of the materials. We characterized the material A16A18 after 5 Henry reaction cycles. ¹³C and ²⁹Si solid state NMR spectra (see ESI[†]) of the used material are nearly unchanged compared to those of the material before use. Furthermore, the characterization of the used material via nitrogen sorption shows a similar shape of the adsorption-desorption isotherms of the material A16A18 before use and after 5 reaction cycles indicating that the architecture did not change significantly (Fig. 5). The slight decrease of the specific surface area from 1120 m² g⁻¹ to 790 m² g⁻¹ can be explained by the repeated mechanical stirring during the reactions and successive filtration steps.

We also examined the use of other substituted aldehydes as substrates in Henry reactions. The use of *p*-bromobenzaldehyde and *p*-anisaldehyde gave the corresponding β -nitroalcohols in 77 and 33% conversion (entries 13/14). These results show that aromatic aldehydes functionalized with electron withdrawing groups are substrates with higher reactivity. Here, p-nitrobenzaldehyde was found to be the most reactive aldehyde in this series. The substitution of the aromatic ring also affects the syn/ anti ratio of the formed β-nitroalcohols. However, the syn diastereoisomer is always preferentially formed in the first reaction cycles using material A16A18.

Ring opening of glycidol

Because of their emulsifying, complexing and lubricating properties, monoglycerides found applications in food, cosmetic, pharmaceutical and textile industries. The ring opening reaction of glycidol with fatty acids (Scheme 5) is the most convenient route for the selective synthesis of monoglycerides. This reaction can be catalyzed by amines and ammonium salts, metal alcoholates or bases. Both silica supported acids and bases have been



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Scheme 5 Monoglyceride synthesis by ring opening of glycidol.

 Table 5
 Conversions in ring opening reactions of glycidol and lauric
 acid using the materials A16A18 and A16A18-p as heterogeneous catalysts

Entry	Catalyst	Conversion (%)	Entry	Solvent	Conversion (%)
1	None	<1	5	A16A18-p	80
2	A16A18	65	6	A16A18-p 2 nd run	72
3	A16A18 2 nd run	61	7	A16A18-p 3 rd run	58
4	A16A18 3 rd run	58	8	A16A18-p 4 th run	65
5	A16A18 4 th run	53			

reported to efficiently promote the formation of monoglycerides by ring opening reactions of glycidol.^{63,64}

Here, we examined the catalytic activity of the amine containing material A16A18 and the ammonium containing material A16A18-p in this reaction. The results of these experiments are summarized in Table 5. It clearly appears that both amine and ammonium functionalized materials promote the reaction and led to lauryl monoglyceride in 65 and 80% yield in the first reaction cycle, respectively. Both materials can be re-used in further reaction cycles but show decreasing catalytic performances with yields of 53% (A16A18) and 65% (A16A18-p) after the 4th re-use. Globally, the ammonium functionalized material A16A18-p shows a slightly higher catalytic activity compared to the amine functionalized material A16A18.

The characterization of the recovered materials by solid state NMR and nitrogen sorption shows that the ring opening reaction of glycidol with fatty acids strongly affects the texture of the materials. After catalysis, the recovered materials show a strongly reduced specific surface area (A16A18: $S_{\text{BET}} < 8 \text{ m}^2 \text{ g}^{-1}$; A16A18-p: $S_{BET} = 92 \text{ m}^2 \text{ g}^{-1}$). Furthermore, the shape of the nitrogen sorption isotherms of the recovered materials indicates that the porous texture collapsed during the successive reaction cycles. This result is supported by X-ray diffraction. The diffractograms of the materials after use as heterogeneous catalysts indicate reduced order in the recovered materials. ¹³C CP-MAS solid state NMR measurements with the used material reveal some degradation of the amine and ammonium substructures under the conditions of the ring opening reaction. However, no Si-C bond cleavage occurs during the reactions as indicated by the complete absence of signals of the Q series in the ²⁹Si CP-MAS spectra of the materials after use. The nitrogen sorption isotherms, X-ray diffractograms and solid state NMR spectra of the recovered materials A16A18 and A16A18-p are given in the ESI[†].

These results show that the ammonium functionalized materials show limited textural and chemical stability under the



Fig. 5 Nitrogen adsorption-desorption isotherms of material A16A18 before (\blacksquare) and after 5 Henry-reaction cycles (×).

conditions of ring-opening reactions. The decreasing catalytic activity of the materials in successive reaction cycles can thus be explained by a collapsed pore structure of the materials and slight chemical degradation of the amine and ammonium substructures. Nevertheless, the new materials are still among the most efficient heterogeneous catalyst systems for these reactions.⁶⁵

5. Conclusion

In conclusion, we report the tuning of the pore size in silica hybrid materials obtained via 'anionic templating' with cationic ammonium precursors. Although the formation mechanism for the generation of these nanostructured silica hybrid phases differs from classical hydrolysis-polyfundamentally condensation methods for the synthesis of PMO type materials and is governed by ionic interactions between the surfactant and the 'organo-cationic' part of the precursor, pore size control was achieved following standard methods, in particular by the addition of swellers (TMB) to the hydrolysis-polycondensation mixtures. This approach appears as a versatile method to tune the morphology in nanostructured silica hybrid materials bearing amine and ammonium groups and allows to obtain materials with pore diameters in the range from 20 to 60 Å.

The original materials appear as versatile organocatalysts for a set of reactions. We show that both amine and ammonium functionalized PMO type materials show interesting catalytic properties and efficiently promote Knoevenagel and Henry reactions. They catalyze also the formation of monoglycerides by ring-opening reactions of glycidol with fatty acids. In this way, amine and ammonium containing PMO materials show interesting features not only concerning the rational design of functional porous solids and materials engineering. Due to their ease of derivatisation, these systems are also interesting for the elaboration of a whole new class of functional materials. In this way, these original functional solids appear as a platform for the development of a large variety of functional catalytic materials. This study highlights the huge potential of *i-silica* materials in this area.

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