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Cooperative Acid–Base Effects with Functionalized Mesoporous Silica Nanoparticles: Applications in Carbon–Carbon Bond-Formation Reactions

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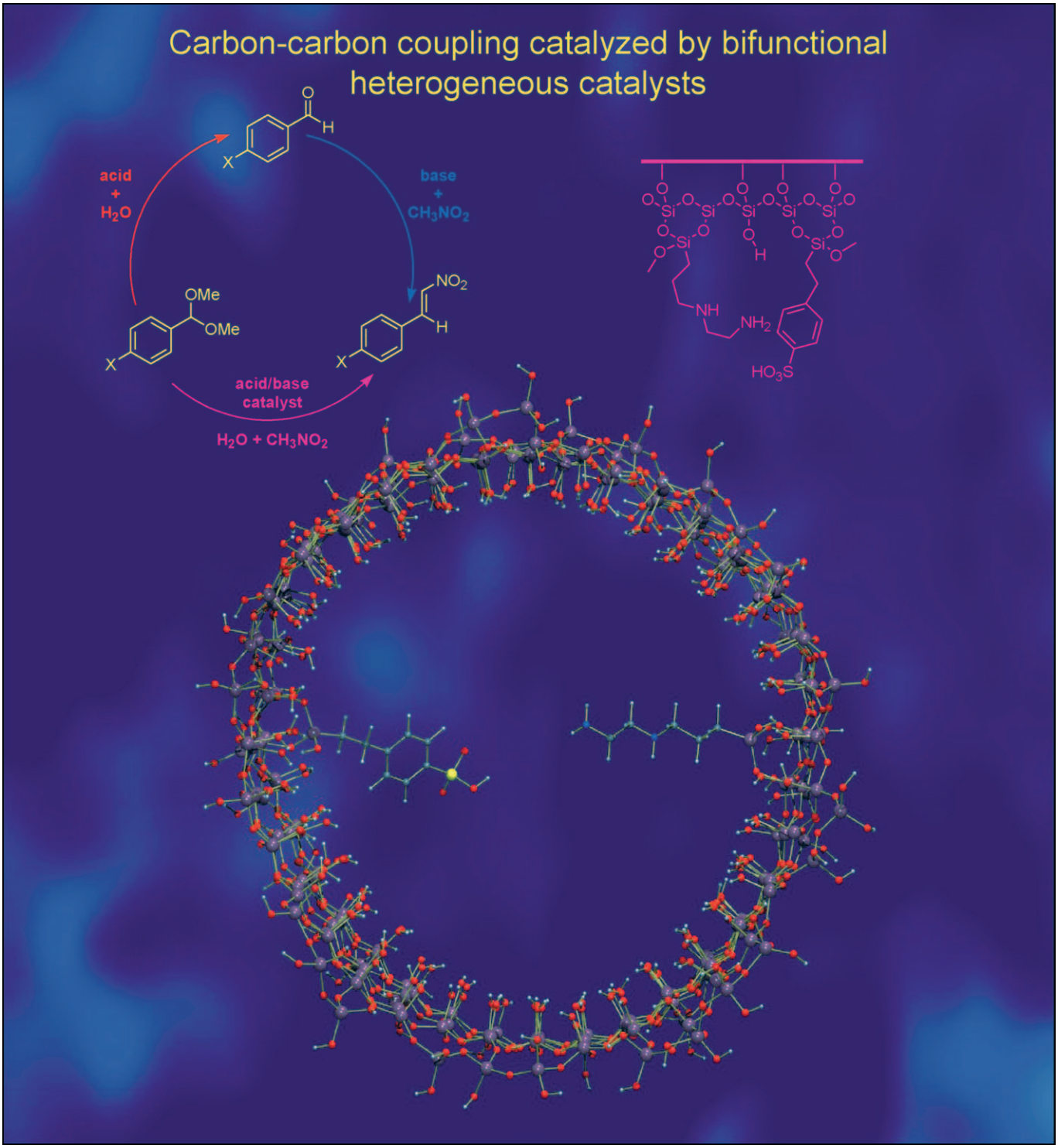

Abstract: Acid–base bifunctional mesoporous silica nanoparticles (MSN) were prepared by a one-step synthesis by co-condensation of tetraethoxysilane (TEOS) and silanes possessing amino and/or sulfonic acid groups. Both the functionality and morphology of the particles can be controlled. The grafted functional groups were characterized by using solid-state ^{29}Si and ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectroscopy, thermal analysis, and elemental analysis, whereas the structural and the morphological features of the materials were evaluated by using XRD and N_2 adsorption–desorption analyses, and SEM imaging. The catalytic activities of the mono- and bifunctional mesoporous hybrid materials were evaluated in carbon–carbon coupling reactions like the nitroaldol reaction and the one-pot deacetalization–nitroaldol and deacetalization–aldol reactions. Among all the catalysts evaluated, the bifunctional sample containing amine and sulfonic acid groups ($MSN–NNH_2–SO_3H$) showed excellent catalytic activity, whereas the homogeneous catalysts were unable to initiate the reaction due to their mutual neutralization in solution. Therefore a cooperative acid–base activation is envisaged for the carbon–carbon coupling reactions.

Keywords: acid–base interactions · C–C coupling · heterogeneous catalysis · mesoporous silica · nanoparticles

Introduction

The control of multistep reaction cascades in complex organic syntheses can be achieved by a systematic development of multifunctional catalysts.[1] In heterogeneous catalysis, multifunctionalization of a given solid support thus requires control of the relative concentrations as well as spatial arrangements of the active sites. This strategy brings to mind biological catalysts. With precisely positioned different active centers, biological systems (enzymes or enzyme complexes) accelerate and control the selectivity of chemical transformations; Lewis acid/base and electrostatic interactions are applied as well as hydrogen and covalent bonding.[2] However, such a synthetic approach of controlling the uniformity and site isolation of multifunctional groups in a solid-state catalyst is by far not trivial and is one of the crucial tasks in heterogeneous catalysis.[3] Nevertheless, by mimicking biological systems, a series of examples has recently been reported wherein the concept of site isolation was applied for the dual activation of electrophiles and nucleophiles by acids and bases on solid supports. For instance, the combination of weak and strong acids such as silanol groups, ureas, or sulfonic acids with various organic bases on solid supports was investigated and synergistic catalytic enhancements were observed.[4] However, systematic investigations as well as the successful cohabitation of organic acid and base functionalities on a single solid support and the evaluation of the catalytic activity of such systems remain elusive for carbon–carbon-bond-forming one-pot reaction cascades.

Mesoporous silicas like MCM-41 that have a high surface area, uniform pore size distributions, tunable morphology, and high thermal stability have inspired considerable research efforts in shape-selective heterogeneous catalysis, separation, ion-exchange processes, and in host–guest chemistry.[5] One important method to modify the physical and chemical properties of mesoporous silicas is to introduce reactive organic groups into the pores of these materials.[6] A precise location of organic functionalities in the mesopores can be realized either by grafting of an organosilicon compound after template removal or by the co-condensation method.[7] To avoid mass-transfer problems not only the extent of organic functionalization but also the morphology of the developed material have to be controlled. Lin et al. and others have demonstrated that silica can be synthesized as uniform mesoporous silica nanoparticles (MSN) and under appropriate conditions these materials can be functionalized with multiple organic groups.[8] The unique morphological features of MSNs—large pore channels (diameter >2 nm) and short diffusion path lengths—are interesting for applications in heterogeneous catalysis since they allow a rapid exchange of substrates and products.[9] The immobilization of catalysts with defined molecular geometries on mesoporous supports with high surface area not only allows a simple catalyst recovery but also enables us to tailor the morphology of the particles as well as the polarity of the channel walls. The latter property is a distinct feature of mesoporous materials in heterogeneous catalysis, thus preferential uptake of a certain substrate inside the nanochannels can be revealed.[10]

Among the organo-functionalized mesoporous compounds, amino-functionalized hybrid materials are well known for their activity in different carbon–carbon coupling reactions.[11] Recent studies, however, showed that the pres-

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ence of surface silanol groups can be beneficial for the catalytic performance when appropriate catalytic functions like amines are introduced inside the pore channels.[12] Moreover, the presence of additional organic functionalities can give rise to enhanced activities by cooperative effects.[13] For instance, the synthesis of bisphenol A from acetone and phenol is a well-established catalytic reaction in which a bifunctional cooperation between sulfonic acid and thiol groups was confirmed.[14] However, the precise positioning of organic acids and bases in one sample of a bifunctional catalyst is a really challenging task due to the incompatible nature of these two functional groups. The most simple approach to such a system is the use of weakly acidic surface silanol sites in cooperative catalysis. However, in this case the relative concentration of the two functional groups as well as their spatial separation, which decides the overall catalytic activity of bifunctional silicas, is almost out of control.

In this paper, we verify in detail the possibility of synthesizing functionalized mesoporous materials possessing different amine groups and of synthesizing bifunctionalized materials possessing amine and sulfonic acid groups. These systems have been investigated as catalysts for various C–C bond-forming reactions such as the nitroaldol (Henry) reaction between substituted benzaldehydes and nitromethane as well as the one-pot deacetalization–nitroaldol and one-pot deacetalization–aldol reactions.

Results and Discussion

Synthesis and spectroscopic characterization of bifunctional MSN samples: In the present study, the co-condensation of different organofunctional groups (acids and bases) with tetraethoxysilane (TEOS) was used to generate hybrid mesoporous silicas. Post-synthetic grafting would lead to a clustering of organic groups, especially in a high-boiling solvent like toluene.[12] The densely packed organic groups would in turn greatly reduce the percentage of silanol groups that can act as weak acid sites for cooperative catalysis. Moreover, such clustering can also reduce the coexistence of acid–base couples for synergetic catalytic reactions.[15] However, the probability of such clustering effects will be reduced for the one-pot synthesized samples and thus well-defined nanocatalysts that have spatially isolated functional groups covalently anchored to the pore walls can be obtained. Aminopropyltrimethoxysilane (APTS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS), 3-(diethylamino)propyltrimethoxysilane (DAPS), and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CSES) were used as precursors and the following mesoporous MSN samples could be generated by using hexadecyltrimethylammonium bromide as surfactant under basic conditions: MSN–NH_2 (containing APTS), MSN–NNH_2 (with AAPTS), MSN–SO_3H (CSES) as well as the bifunctional acid–base-containing materials MSN–NH_2–SO_3H (APTS+CSES) and MSN–NNH_2–SO_3H (AAPTS+CSES).

Solid-state NMR spectroscopy was used to obtain spectroscopic evidence for the presence of the desired organic functional groups in the particles as well as to confirm the chemical structure and relative concentrations. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra of monofunctionalized MSN–NH_2, MSN–NNH_2, and MSN–SO_3H as well as those of bifunctionalized MSN–NH_2–SO_3H and MSN–NNH_2–SO_3H are presented in Figure 1. These

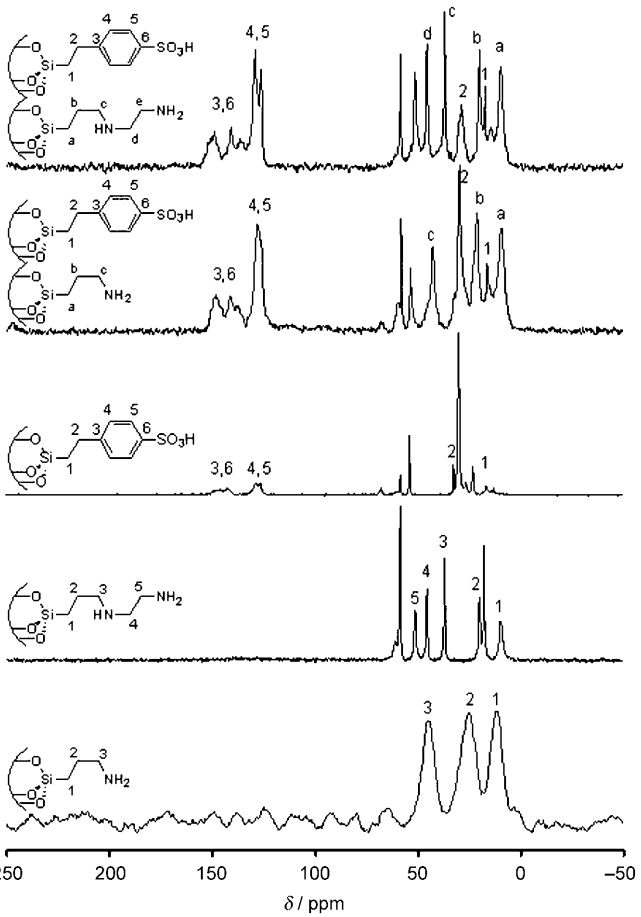


Figure 1. ^{13}C CP/MAS NMR spectra of functionalized MSN samples. The unmarked signals denote residual surfactant peaks and ethoxy groups.

spectra prove the grafting of the functional groups and the absence of residual surfactant species. The observed chemical shifts of the organic groups agree well with those of the corresponding organosilane precursors measured in solution. The peak assignments are mentioned in Figure 1. The absence of signals in the range of $\delta = 50$–70 ppm indicates that the surfactant was removed from the solids by extraction, whereas the presence of weak bands at $\delta = 15$ and 58 ppm relates to the presence of $SiO\text{-}CH_2\text{-}CH_3$ species that may arise from an incomplete hydrolysis of the silylating agents or from an esterification reaction between Si–OH groups and ethanol during the extraction process.[16]

The presence of organic functional groups was further verified by solid-state ^{29}Si MAS NMR spectroscopy. Peaks

at $\delta = -110$, -100, -91, -66, and -58 ppm were assigned to the Q^4 ($Si(OSi)_4$), Q^3 ($Si(OH)(OSi)_3$), Q^2 ($Si(OH)_2(OSi)_2$), T^3 ($SiR(OSi)_3$), and T^2 ($Si(OH)R(OSi)_2$) sites, respectively (Figure 2).[16] The presence of T^3 and T^2 functionalities confirms a strong covalent linkage between the organic groups and the silica surface. The surface coverage (SC) of the mesopores with organic groups could be estimated as $SC = (T^2+T^3)/(T^2+T^3+Q^2+Q^3)$ and the results are depicted in Table 1. The total concentration of organic functional groups (organic acid and bases) in MSN–NH_2–SO_3H and MSN–NNH_2–SO_3H are 0.76 and 0.69 mmol g^{-1} and the concentration ratios of acid/base are 0.59 and 0.47 mmol g^{-1}, respectively, from elemental analysis.

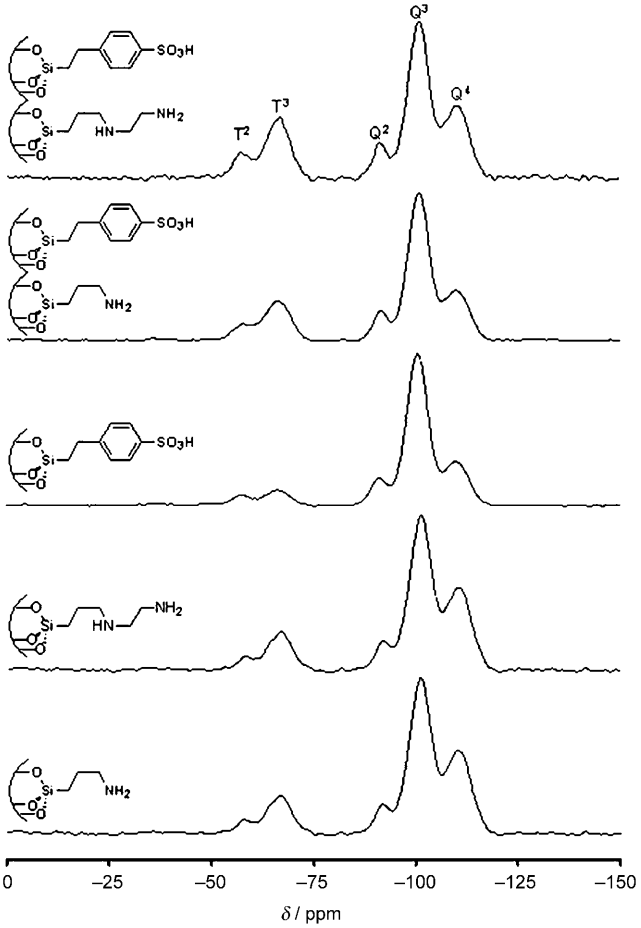


Figure 2. ^{29}Si CP/MAS NMR spectra of the functionalized MSN samples.

Two distinct weight losses are observed in the thermogravimetric analysis (TGA) patterns indicating the removal of physisorbed water/ethanol residing in the pore channels (< 120 °C) as well as the decomposition of organic groups (200–600 °C) functionalized inside the pore channels of the MSNs (Figure 3A, Table 1).

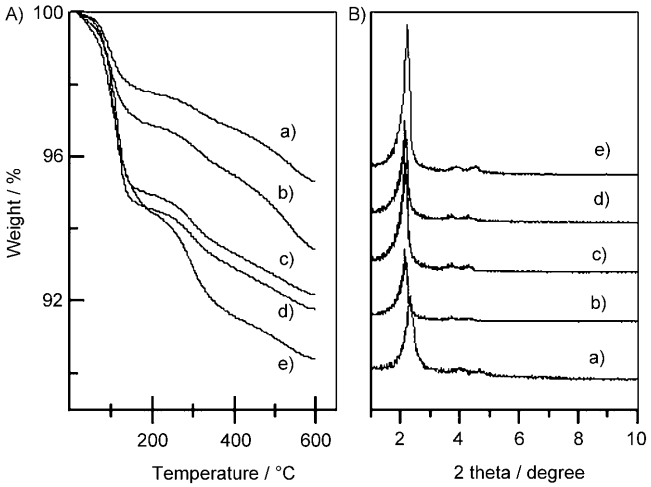


Figure 3. A) TG plots of a) MSN–NH_2, b) MSN–NNH_2, c) MSN–SO_3H, d) MSN–NH_2–SO_3H, and e) MSN–NNH_2–SO_3H. B) Powder XRD patterns of a) MSN–NH_2, b) MSN–NNH_2, c) MSN–SO_3H, d) MSN–NH_2–SO_3H, and e) MSN–NNH_2–SO_3H.

Structural characterization: The XRD patterns of the MSN samples after the surfactant has been removed show a sharp (100) Bragg reflection with additional peaks corresponding to the (110) and (200) reflections, typical for ordered mesoporous materials like MCM-41 that have *p6mm* mesostructures (Figure 3B). In comparison with the other MSN samples, MSN–NH_2 and MSN–NNH_2 exhibit less-intense reflections in the powder XRD, which indicates a slightly disordered pore structure.

The N_2 adsorption–desorption analyses exhibit type IV isotherms with a capillary condensation step in the low-pressure region and an almost constant adsorption in the high-pressure region, which again proves the existence of uniform mesopores (Figure 4A). Again MSN–NH_2 and MSN–NNH_2 are different: a decreased uptake of nitrogen can be noted for these samples, which confirms their slightly disordered pore structures. It should be mentioned at this point that the interactions between the organosilanes and the surfactant molecules during the micelle formation and the gelation determine the properties of the

Table 1. Structural and textural properties of organic-group-functionalized MSN samples.

	wt loss [%][a]	S_{BET} [$m^2 g^{-1}$]	Pore size [nm]	V_{pore} [$cm^3 g^{-1}$]	SC[b]	TOG[c] [mmol g^{-1}]
MSN–NH_2	3.8	456	2.42	0.68	22	0.42
MSN–NNH_2	4.1	534	2.29	0.71	19	0.32
MSN–SO_3H	6.5	564	2.25	0.63	16	0.35
MSN–NH_2–SO_3H	7.8	673	2.27	0.65	26	0.76
MSN–NNH_2–SO_3H	9.6	523	2.24	0.61	23	0.69
MSN	2.4	695	2.53	0.58	–	–

[a] Weight loss between 200 and 600 °C, obtained from TG analysis. [b] Surface coverage determined from ^{29}Si MAS NMR analysis. [c] Total amount of organic groups, determined from elemental analysis.

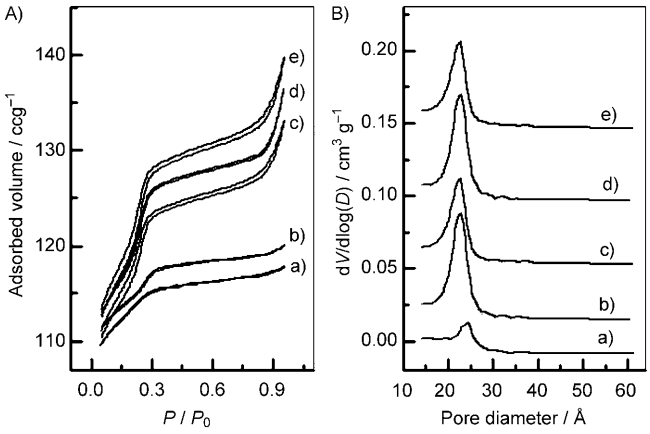


Figure 4. A) N_2 adsorption–desorption isotherms and B) pore size distribution plots of a) MSN–NH_2, b) MSN–NNH_2, c) MSN–SO_3H, d) MSN–NH_2–SO_3H, and e) MSN–NNH_2–SO_3H.

materials. These interactions in turn depend on the nature of the organic groups present in the organosilanes and synthesis procedure.[17] The narrow and sharp pore size distribution curves (Figure 4B) calculated from the Barrett–Joyner–Halenda (BJH) model suggest that the mesopores are uniform. The textural properties such as BET surface area (S_{BET}), pore volume, and pore size observed for all the surfactant-extracted samples are summarized in Table 1.

Morphological studies: The morphology of the obtained mono- and bifunctional MSN particles was examined by using field emission scanning electron microscopy (FESEM) imaging (Figure 5). The particles developed in this work are highly monodisperse and their average particle diameters vary between 300 nm and 1 μm. The images further show that the different organic groups have a dramatic influence on the size and the shape of the mesoporous silica particles. For instance, the MSN–NH_2 sample shows slightly curved, tubular-shaped particles that have a mean length of approximately 1 μm. Changing the amine groups from APTS to AAPTS does not change the particle morphology severely, while the length of the tubes decreases to about 600 nm, accompanied with a reduction of the particle diameter. In sharp contrast, addition of CSES to APTS completely changed the morphology of the materials. MSN–NH_2–SO_3H consists of spherical particles that have a mean diameter of 300–400 nm, similar to the MSN–SO_3H sample, whereas for MSN–NNH_2–SO_3H bean-shaped particles of approximately 500 nm diameter are observed. In general, the particle size of the bifunctional mesoporous materials appears significantly lower than that of the monofunctionalized amine samples, which yielded elongated particles. Lin and co-workers suggested that under the highly alkaline conditions of the co-condensation reaction, the trialkoxyorganosilanes are hydrolyzed and converted into trihydroxyorganosilanes, which means that the head of the molecule is always hydrophilic, whereas the tail is either hydrophilic or hydrophobic. The interaction of this part of the organosilane molecule with the surfactant used for the micelle formation will probably decide the overall morphology of the developed sample.[8] The nature of these interactions can be electrostatic attraction/repulsion, hydrogen bonding, and hydrophobic/hydrophilic. They arise from the intrinsic molecular properties of the organosilane itself.

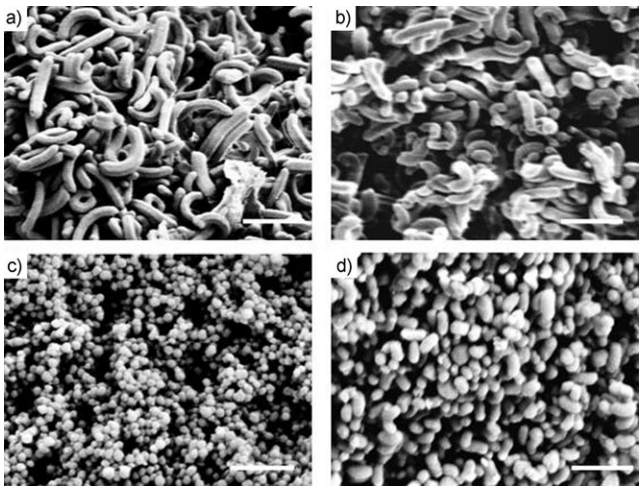
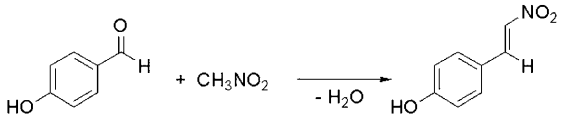


Figure 5. FESEM images of a) MSN–NH_2, b) MSN–NNH_2, c) MSN–NH_2–SO_3H, and d) MSN–NNH_2–SO_3H (scale bar = 1 μm).

Catalytic studies: To investigate how the intrinsic functionalities of the organic/inorganic hybrid catalysts work cooperatively, three different sets of reactions were evaluated: a nitroaldol reaction, a one-pot deacetalization–nitroaldol reaction, and a one-pot deacetalization–aldol reaction. The condensation of nitroalkanes with carbonyl compounds, the so-called Henry reaction, is a well-established and thoroughly verified chemical procedure to generate nitroalkenes, which are, for example, of importance for the synthesis of pharmaceutical products.[18] However, selective formation of a nitroalkene using conventional strong bases is difficult to achieve since the conjugate addition of the nitroalkane to the C–C double bond of the nitroalkene gives bis-nitro compounds in a side reaction.[19] This was our motivation to investigate the catalytic performance of the aforementioned mesoporous materials in this reaction. The catalytic data obtained from the different organofunctionalized MSN samples in the Henry reaction of *p*-hydroxybenzaldehyde and nitromethane (Scheme 1) are summarized in Table 2.

The amount of catalyst used for each experiment was determined on the basis of the loading of the hybrid materials with organic groups to ensure that similar amounts of amine



Scheme 1. Nitroaldol reaction of *p*-hydroxybenzaldehyde and nitromethane.

Table 2. Catalytic nitroaldol reaction with different catalysts.[a]

Entry	Catalyst	t [h]	Yield [%][b]
1	MSN–NH_2	6	33
2	MSN–NNH_2	6	44
3	MSN–NEt_2	12	trace
4	MSN–SO_3H	12	0
5	MSN–NH_2–SO_3H	6	60
6	MSN–NNH_2–SO_3H	6	96 (94)[c]
7[d]	MSN–NNH_2 + MSN–SO_3H	6	54
8[e]	MSN–NNH_2–SO_3H	4	100
9[f]	Sil–MSN–NNH_2–SO_3H	6	0
10	MSN–NNH_2–Cl	6	71
11[g]	MSN	12	0
12	MSN–NNH_2–SO_3H + *p*-toluene sulfonic acid	6	trace
13	MSN–NNH_2–SO_3H + *n*-hexylamine	6	55
14	*p*-toluene sulfonic acid + *n*-hexylamine	6	0

[a] Reaction conditions: *p*-hydroxybenzaldehyde (1 mmol), CH_3NO_2 (10 mL), 90 °C. [b] Determined by GC–MS analysis, based on the aldehyde. [c] Yield for the third reuse of the catalyst. [d] 1:1 physical mixture of acid and base. [e] Using 5.6 mmol of CSES. [f] Silylated sample. [g] Using a 50 mg sample.

groups (molar ratio of aldehyde/amine = 40) were present. Otherwise a comparison of the results would be difficult. Since acidic groups play a vital role in the imine formation as well as in the subsequent nucleophilic attack by nitromethane it was anticipated that highly acidic sites like sulfonic acids (maybe together with the weakly acidic surface silanol groups) might effectively activate the acceptor substrates in a cooperative effect.[20]

According to the requirements of this C–C coupling reaction, it was found that bifunctionalized samples give considerably higher conversions than the monofunctionalized ones containing only primary amines. The combination of sulfonic acid and amines gives good to excellent conversions and it is worth noting that the MSN–NNH_2–SO_3H sample showed an even higher conversion than the MSN–NH_2–SO_3H sample (Table 2, entry 5 vs. 6). The improved catalytic activity of MSN–NNH_2–SO_3H relative to MSN–NH_2–SO_3H may arise from a better activation of the substrates by the facilitation of the nucleophilic attack at the imine carbon atom due to the presence of a more flexible diamine group or due to differences in the morphology of the materials. Further experiments may, however, be required to determine the contribution of each. Furthermore, the tertiary amine (DAPS)-functionalized MSN–NEt_2 catalyst (entry 3) exhibits poorer catalytic performance for the nitroaldol reaction than the catalyst MSN–NH_2 with the primary amine, despite the stronger basicity of the alkyl-substituted tertiary amine. Control experiments with a pristine MSN sample displayed no catalytic activity at all (entry 11), which indicates that it is not the silica surface itself but the surface-bound organic functional groups that are responsible for the catalytic transformation. A physical mixture of acid- and base-containing MSN silica (MSN–NNH_2 + MSN–SO_3H; entry 7) showed an intermediate level of conversion, however, significantly lower than the conversion obtained from the bifunctionalized acid–base-containing MSN catalyst (entry 6). These results illustrate that it is favorable to have the immobilized acid and base groups in close proximity to each other to realize cooperative catalytic enhancements. The MSN–SO_3H sample did not show any catalytic activity at all (entry 4) revealing that the presence of the amine functionality is crucial for the reaction to be initiated. The addition of equivalent amounts of *p*-toluenesulfonic acid or *n*-hexylamine to MSN–NNH_2–SO_3H results in a pronounced drop of activity (entries 12 and 13), since these species destroy the acidic/basic sites on the surface. A homogeneous mixture of these two components in the complete absence of MSN–NNH_2–SO_3H shows no activity at all (entry 14), as expected.

To further evaluate the role of the two components in the cooperative catalysis, we examined the catalytic activity of MSN–NNH_2–SO_3H using various ratios of CSES in the gel mixture. With an increase in the percentage of $-SO_3H$ groups, the conversion rate increases, which suggests that the aldehyde is activated preliminarily by the acid groups and this facilitates the formation of imines by the immobilized amine groups (entry 8). However, the enhanced catalytic activity observed for the bifunctionalized MSN sample might either be due to the presence of silanol groups or due to sulfonic acid groups (or a combination of both). To verify this hypothesis, the residual silanol groups were capped by phenyl groups by reaction with phenyltrimethoxysilane in toluene. FTIR spectroscopy investigations show that after immobilization of the phenyl groups the silanol density is decreased (Figure 6c). This silylation has a pronounced negative effect on the catalytic performance: after removal of silanol groups from MSN–NNH_2–SO_3H the reaction did not start (Table 2, entry 9). Alternatively, the $-SO_3H$ groups in the MSN–NNH_2–SO_3H sample were replaced by simple chloropropyl groups (MSN–NNH_2–Cl), since these functionalities will not activate the electrophile as the acid groups do. Accordingly, a decrease in conversion was noted for the MSN–NNH_2–Cl sample (entry 10). These results together with the other data presented in Table 2 suggest that a cooperative effect between the amine groups and the acidic

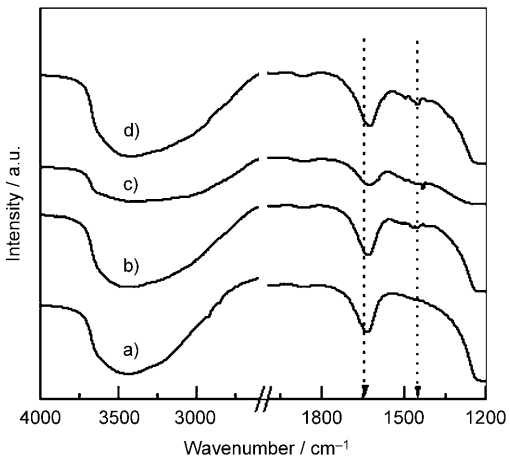


Figure 6. FTIR spectra (KBr) of a) MSN, b) MSN–NNH_2–SO_3H, c) silylated-MSN–NNH_2–SO_3H, and d) MSN–NNH_2–SO_3H treated with benzaldehyde.

sites—derived from silanols and sulfonic acids—must exist in which the sulfonic acid groups alone cannot enhance the reaction. This may be due to the lower content of this acidic group compared with the surface silanol groups.

To evaluate substrate effects, a series of different aldehydes were used for the Henry reaction with MSN–NNH_2–SO_3H as the catalyst (Table 3). It is worth noting that all substrates gave the *para*-substituted nitrostyrene product exclusively, except *p*-nitrobenzaldehyde and *p*-chlorobenzaldehyde, which gave a mixture of the nitroalcohol and nitrostyrene. The formation of nitroalcohols using *para*-nitro- or *para*-chlorobenzaldehyde as the substrate may arise from the presence of the electron-withdrawing groups in the aldehyde, which might partly prevent the dehydration reaction of the nitroalcohols. The conversions vary according to the electron-donating or -withdrawing properties of the substituents in the *para* position. In general the yields are higher for more electron-rich aromatic aldehydes. Furthermore, positioning the electron-donating group on the *ortho* position of the aldehyde decreased the yield of the nitroalkene product probably due to the steric blockage at the aldehyde position (entry 8).

Table 3. Application of different aldehydes in the catalytic nitroaldol reaction.[a]

Entry	Substrate	Yield [%][b]
1	benzaldehyde	89
2	*p*-hydroxybenzaldehyde	96
3	*p*-methoxybenzaldehyde	90
4	*p*-butoxybenzaldehyde	84
5	*p*-nitrobenzaldehyde	38 (68:32)[c]
6	*p*-chlorobenzaldehyde	54 (33:67)[c]
7	*p*-carboxybenzaldehyde	trace
8	*o*-hydroxybenzaldehyde	trace
9	octanal	25

[a] Reaction conditions: aldehyde (1 mmol), CH_3NO_2 (10 mL), catalyst MSN–NNH_2–SO_3H (0.025 mmol amine), 90 °C, 6 h. [b] Determined by GC–MS analysis, based on aldehyde. [c] Ratio of nitroalcohol/nitroalkene.

Even though the yield of the nitrostyrene product correlates with the electronic situation of the aldehydes, no significant difference was noted for reactions carried out with 1:1 molar mixtures of different *p*-substituted reactants using the MSN–NNH_2 catalyst. For example, combinations of *p*-hydroxybenzaldehyde and different alkoxy benzaldehydes were attempted in which no preference towards a particular substrate was observed when the mesopores were decorated solely with hydrophilic groups (namely, AAPTS and silanols). Nevertheless, by analyzing the molar ratio between the products an increase of the conversion for *p*-hydroxybenzaldehyde was noted for the MSN–NNH_2–SO_3H catalyst (Table 4). This is probably due to a steric effect: The benzaldehyde with the large *p*-butoxy substituent (entry 2) is consumed less favorably than the aldehyde with the smaller *p*-methoxy substituent (entry 1).

Table 4. Competitive nitroaldol reactions with MSN–NNH_2–SO_3H catalyst.[a]

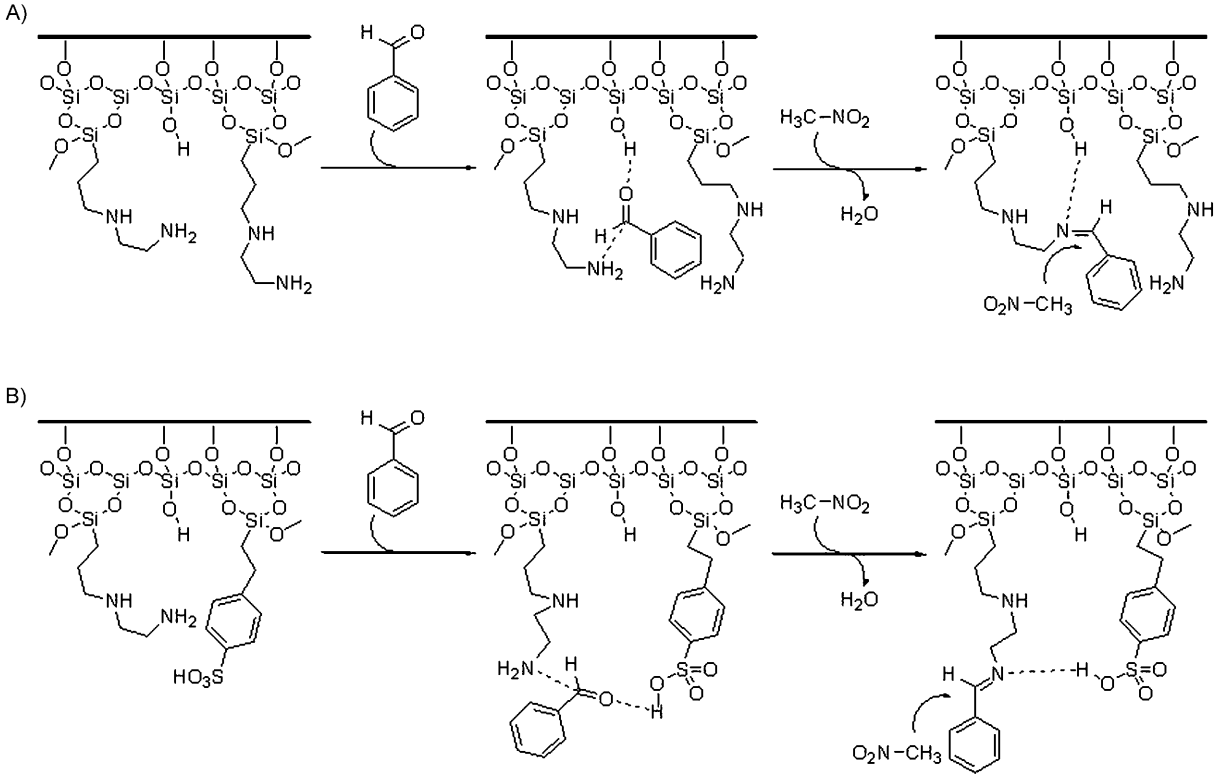
Entry	Substrate	Product ratio
1	*p*-hydroxybenzaldehyde/*p*-methoxybenzaldehyde	1.8
2	*p*-hydroxybenzaldehyde/*p*-butoxybenzaldehyde	2.3
3	*p*-hydroxybenzaldehyde/*p*-methylbenzaldehyde	1.5
4	*p*-hydroxybenzaldehyde/*p*-nitrobenzaldehyde	1.3

[a] Reaction conditions: aldehydes (1 mmol), CH_3NO_2 (10 mL), 90 °C, 6 h.

To get a better insight into the nature of the reaction intermediates, FTIR spectra of MSN–NNH_2–SO_3H after treatment with a solution of benzaldehyde were recorded. The strong and broad absorption resulting from the MSN support (1600–1690 cm^{-1}) does not allow the detection of the C=N stretching vibrations of the imine at 1640 cm^{-1}. However, new peaks appeared at 1452 cm^{-1} for the C–C vibrations of benzylimine species. The formation of an imine was also confirmed by the yellow color of the solid samples after the reactions.[21,22] Because imine intermediate formation from -NH_2 groups and the aldehyde generally occurs very fast, the rate-determining step in the nitroaldol reaction should be the addition of nitroalkanes to the imine intermediate.[4k]

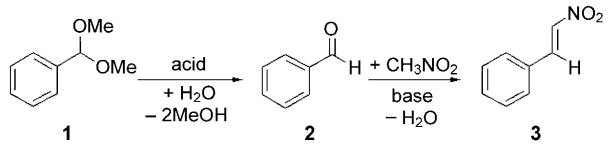
Since the two antagonist organic functional groups (acid and base) were added sequentially to the TEOS/surfactant gel mixture, it is reasonable that there would be neighboring acid–acid, base–base, and acid–base sites. If the catalytic activity arises entirely due to base–base or acid–base (amine–silanol) interactions, the conversion should be higher for MSN–NNH_2 than MSN–NNH_2–SO_3H. Considering the excellent catalytic activity of MSN–NNH_2–SO_3H relative to the monofunctionalized samples and their physical mixtures it can be surmised that a clustering of organic amino groups in the pores of the materials cannot be dominant. In contrast, a majority of the basic sites must exist in close proximity to acidic sites (sulfonic acid or silanol), otherwise no cooperative effects can occur. Thus, the probable mechanism for the nitroaldol reaction involves a dual activation of electrophiles and nucleophiles at the amine base sites and the neighboring acid sites (silanols and sulfonic acids) in which 1) the aldehyde gets activated by the surface acidic sites, which allows the immobilized $-NH_2$ groups to attack the carbonyl group of the aldehyde, 2) the imine is formed by a dehydration reaction, and 3) the nitroalkane reacts with the activated imine to form the nitroalkene product (Scheme 2). The decreased yield of the nitroalkenes in the presence of the MSN–NEt_2 sample also supports the conclusion given above. Thus, due to the superior activity of MSN–NNH_2–SO_3H compared with MSN–NNH_2 it seems that the sulfonic acid groups are more efficient activators than the silanol moieties.

The results of the Henry reaction shown above suggest that the organic acids and bases must be in close proximity for a catalytic enhancement. For a further proof of the concept, the one-pot synthesis of 2-nitrovinyl benzene (**3**) from nitromethane and benzaldehyde dimethyl acetal (**1**) was



Scheme 2. Reaction mechanism for the formation of nitroalkenes in A) MSN–NNH_2 and B) MSN–NNH_2–SO_3H.

evaluated by using different mono- and bifunctionalized MSN catalysts (Scheme 3, Table 5). This reaction cascade involves two separate reactions: an acid-catalyzed deprotection of **1** to yield benzaldehyde followed by the base-catalyzed nitroaldol reaction in nitromethane to yield **3**. Deacetalization is used to recover protected aldehydes in organic chemistry.[23] Remarkably, the bifunctionalized MSN–NNH_2–SO_3H and MSN–NH_2–SO_3H samples convert **1** to **3** in quantitative yields after 5 h (entries 1, 3, and 5). With MSN–SO_3H as the catalyst and therefore in the absence of any amino groups, benzaldehyde is the sole product (entry 6). Only a negligible formation of **3** was noted in the presence of MSN–NNH_2 (entry 7). Thus each catalyst on its own is unable to promote the conversion of **1** to **3** in quantitative yields indicating a tandem action of the bifunctionalized catalysts, similar to biological systems. In addition, the reaction sequence was unable to be completed when the reaction was carried out at room temperature, which shows the necessity of high temperatures for the formation of the nitroalkene products (entry 2). Thus the formation of the nitroaldol product (**3**) was anticipated to arise by way of a sulfonic acid catalyzed deacetalization reaction, followed by a nitroaldol reaction of nitromethane with benzaldehyde, as explained earlier. Interestingly, it can be noted that this one-pot reaction does not require the addition of water, probably due to the presence of adsorbed water in the internal pore channels of MSN materials and/or the successive production of water during the nitroaldol reaction (entry 3).



Scheme 3. One-pot deacetalization–nitroaldol cascade reaction.

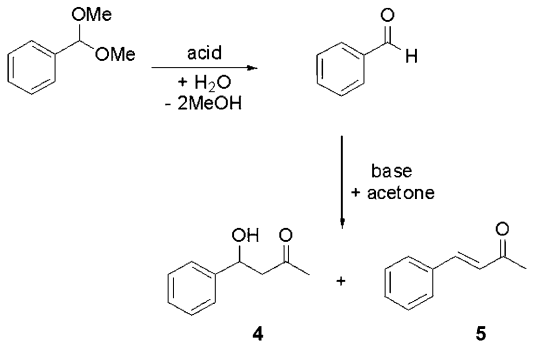
Table 5. One-pot deacetalization–nitroaldol cascade reaction.[a]

Entry	Catalyst	Conv. of **1** [%]	Yield of **2** [%]	Yield of **3** [%]
1	MSN–NNH_2–SO_3H	98	5	95
2[b]	MSN–NNH_2–SO_3H	34	100	0
3[c]	MSN–NNH_2–SO_3H	97	8	92
4	Sil–MSN–NNH_2–SO_3H	53	73	27
5	MSN–NH_2–SO_3H	55	32	68
6	MSN–SO_3H	100	100	0
7	MSN–NNH_2	trace	trace	trace
8	MSN–NNH_2–SO_3H + *n*-butylamine	trace	trace	trace
9	MSN–NNH_2–SO_3H + *p*-toluene sulfonic acid	100	100	trace
10	MSN	trace	trace	0

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), CH_3NO_2 (5 mL), 90 °C, 5 h. [b] At room temperature. [c] Without the addition of water.

In a similar way, the catalytic tandem conversion of benzaldehyde dimethyl acetal to aldol products (deacetalization–aldol) was evaluated in which the electrophile was

changed from nitromethane to acetone. This reaction pathway also includes two separate steps: the acid-catalyzed deprotection of benzaldehyde dimethyl acetal to yield benzaldehyde followed by the base-catalyzed aldol condensation reaction (Scheme 4, Table 6). Similar to the reaction shown



Scheme 4. One-pot deacetalization–aldol cascade reaction.

Table 6. One-pot deacetalization–aldol cascade reaction.[a]

Entry	Catalyst	Conv. of **1** [%]	Yield of **5** [%]
1	MSN–NNH_2–SO_3H	58	40
2	MSN–NH_2–SO_3H	51	28
3	MSN–SO_3H	63	trace
4	MSN–NNH_2	8	24
5	MSN	trace	0

[a] Reaction conditions: benzaldehyde dimethyl acetal (1 mmol), $(CH_3)_2CO$ (5 mL), 50 °C, 24 h.

above, the bifunctional MSN–NNH_2–SO_3H sample showed better catalytic conversions to yield the aldol product (dehydrated product, **5**), whereas the monofunctionalized samples were unable to complete the reaction process, which again confirms the acid–base cooperativity that exists in the bifunctional MSN samples.[24]

The recyclability of the bifunctional catalyst MSN–NNH_2–SO_3H was examined by isolating it from the reaction mixture (centrifugation, washing with ethanol and dichloromethane, and drying). Due to the tight anchoring and the spatial separation of the organic functional groups, the catalyst showed almost no loss in activity in the third run (Table 2, entry 6). Additionally, the ^1H NMR spectroscopic analysis of the reaction filtrate gave no hint of leaching of the immobilized organic groups and the elemental analysis of the recovered catalyst confirmed the retention of the organic content on the mesoporous surface.

Conclusion

As a central result, we were able to prove that organic functional groups that cannot coexist in solution can effectively be utilized for cooperative catalytic reactions by immobilizing such groups on high-surface-area supports and by controlling their spatial arrangements. Even though the latter property cannot be controlled completely due to limitations of the synthesis, a pronounced enhancement of the catalytic activity can be realized relative to the individual counterparts. The successful cohabitation of organic amines and organic acids on high-surface-area solid supports ensures a high catalytic activity and a simple catalyst recovery as shown for a series of C–C bond-formation reactions. We envisage that a successful cohabitation of antagonist groups like acids and bases within a material can open the way to new routes for the rational design of morphology-controlled novel nanomaterials for multifunctional applications.

Experimental Section

General: X-ray powder diffraction (XRD) patterns were obtained on a Siemens D5005 diffractometer with $Cu_{K\alpha}$ radiation. Nitrogen adsorption–desorption isotherms were measured at 77 K on a Quantachrome Autosorb 1 sorption analyzer after evacuation of the samples at 120 °C overnight. The specific surface areas were calculated by means of the Brunauer–Emmett–Teller (BET) equation in the low relative pressure interval (<0.3) and the pore size distribution curves were analyzed with the adsorption branch by the BJH method. ^{13}C CP/MAS and ^{29}Si CP/MAS NMR spectra were recorded on a Bruker DSX Avance spectrometer at resonance frequencies of 100.6 and 79.5 MHz, respectively. The infrared spectra were recorded by using a Jasco FT/IR-6100 spectrometer. The morphology of the mesoporous particles were determined by a field emission scanning electron microscope with 10 kV acceleration voltage and 0.005 nA beam current. The reaction product was analyzed by GC–MS (Varian).

Tetraethoxysilane (TEOS, 99%), cetyltrimethylammonium bromide (C_{16}TAB, 95%), and organoalkoxysilanes (APTS, AAPTS, DAPS, CSES) were purchased from Aldrich chemicals. The aldehydes, benzaldehyde dimethyl acetal, and nitromethane were purchased from Acros. All chemicals were used as received without further purification.

Synthesis of bifunctionalized MSN silicas: In a typical synthesis, C_{16}TAB (2.0 g, 5.4 mmol) was dissolved in deionized water (480 g) containing 2 M NaOH (7 mL) under stirring at room temperature. The temperature of the solution was then raised to 80 °C and the solution became clear after 30 min. To this clear solution, TEOS (9.2 g, 44.8 mmol) and the desired organoalkoxysilane (2 mmol) were added sequentially. For the synthesis of MSN–NNH_2–SO_3H, CSES (2 mmol) dissolved in dichloromethane (50/50 w/w) was added followed by the addition of AAPTS (2 mmol) under vigorous stirring. White precipitates were obtained after approximately 3 min. The mixtures were then stirred for another 4 h. The products were then separated by hot filtration, washed with water, and extracted with a mixture of HCl/EtOH (0.3 g/100 mL) at 60 °C for 6 h to remove the surfactant and to convert $-SO_3Na$ to $-SO_3H$ species. The resulting white solid products were filtered, washed with water and then ethanol, and dried under vacuum.

Nitroaldol reaction: A mixture of the aldehyde (1 mmol), nitromethane (10 mL), and the selected catalysts (molar ratio of aldehyde/amine = 40) were kept at 90 °C under magnetic stirring. The reaction mixture was then stirred under an atmosphere of nitrogen and aliquots of the sample mixture were removed with a filter syringe and evaluated by GC–MS to determine the yield of the nitrostyrene product.

One-pot deacetalization–nitroaldol reaction: A mixture of benzaldehyde dimethyl acetal (1 mmol), nitromethane (5 mL), and the mesoporous catalyst (0.025 mmol of amine) was kept at 90 °C under magnetic stirring. The reaction mixture was then stirred under a nitrogen atmosphere for 5 h and the sample mixture was removed with a filter syringe and evaluated by GC–MS to determine the yield of 2-nitrovinylbenzene.

One-pot deacetalization–aldol reaction: A mixture of benzaldehyde dimethyl acetal (1 mmol), acetone (5 mL), and the mesoporous catalyst (0.05 mmol of amine) were kept at 50 °C under magnetic stirring. The re-

action mixture was then stirred under a nitrogen atmosphere for 24 h and the filtrate was analyzed by GC–MS and ^{1}H NMR spectroscopy to determine the yield of the aldol condensation products.

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