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Hybrid Inorganic-Organic Materials Carrying Tertiary Amine and Thiourea Residues Tethered on Mesoporous Silica Nanoparticles: Synthesis, Characterization, and Co-Operative Catalysis

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Abstract: Mesoporous silica nanoparticles carrying different loadings of tertiary amine and thiourea residues (residues ratios 53/47, 68/32, and 22/78, respectively) were synthesized by the co-condensation method and fully characterized by CP MAS NMR, powder XRD, SEM, BET, BJH and FT-IR techniques. These materials were tested as bifunctional catalysts in the conjugate addition of acetylacetone to 2-nitrostyrene, a reaction that under solvent-free conditions occurred in quantitative yield. By carrying out several experiments with the bifunctional catalysts featuring different molar ratios of active sites, and with different combinations of monofunctional supported and non-supported catalyst, the co-operativity of the tertiary amine and thiourea residues in catalyzing the reaction was demonstrated. The use of the bifunctional catalyst was extended to the addition of acetylacetone to an activated imine. Catalyst recycling for a total of three reaction cycles was demonstrated without significant erosion of activity.

Keywords: catalyst recycling; co-operative catalysis; mesoporous materials; organic catalysis; organic-inorganic hybrid composites

Introduction

The catalytic efficiency of enzymes largely relies upon co-operative interactions of functional groups synergistically at work in the active site. In the attempt at mimicking enzymatic catalysis with simpler molecules, the concept of co-operative catalysis has been implemented in the design of artificial catalytic systems, mostly by assembling bifunctional catalysts on different scaffolds. These can be structures of widely different properties and complexity, ranging from short chains of carbon atoms to organic or inorganic macroscopic materials. The selection of the scaffold, which has the very important task of keeping the catalysts in the correct relative disposition required for co-operativity and of providing a favourable reaction environment, is crucial to the success of the design.

Recently, a limited number of bifunctional catalysts supported on mesoporous silica have been reported.[1] As a support, mesoporous silica takes advantage both of the large pore size of the nanoparticles (≥ 2 nm), that allows easy mass transfer, and of ready functionalization with different organic residues.[2] Among the synthetic protocols investigated to obtain mesoporous silica-supported catalysts, co-condensation appears superior to post-synthetic grafting, especially when, as in the case of co-operative catalysis, inorganic-organic hybrid materials carrying different catalytic residues must be obtained.[3] In addition, the nature of the co-condensation process, that involves the reaction of a tetralkoxysilane with trialkoxyorganosilanes carrying the different functionalities required for catalysis, can open access to systems in which the functional group ratios can be varied at will, allowing an additional tuning of the catalyst's properties. This approach can also benefit extensively from the great number of organocatalysts that have recently become available both in the soluble[4] and in the supported form.[5]

According to a recent review,[1] co-operativity[6] of bifunctional catalysts supported on mesoporous silica has been demonstrated so far only by the groups of Lin[7] and Davis.[8] In particular, Lin and his co-workers synthesized a catalyst featuring secondary amine and urea residues, and showed that this system promoted the addition of acetone, nitromethane, and trimethylsilyl cyanide to 4-nitrobenzaldehyde, possibly by co-operative activation of the aldehyde carbonyl by H-bonding with urea and of the nucleophiles by the secondary amine. Davis and his collaborators reported co-operation of sulfonic acids with thiol groups in the bisphenol A synthesis and of Brønsted acids (sulfonic, phosphonic, and carboxylic acids) with primary amine residues in the aldol reaction.

Herein, we report the synthesis and complete characterization of a new bifunctional catalytic system supported on mesoporous silica featuring tertiary amine and thiourea functionalities in different ratios. The co-operativity of the active sites of this system has been demonstrated in the conjugate addition of acetylacetone to 2-nitrostyrene, a reaction occurring in quantitative yield when performed under solvent-free conditions. The same catalyst was also demonstrated to be active in the addition of acetylacetone to *N*-carbobenzyloxybenzaldimine. Preliminary experiments also showed that catalyst recycling was possible.

Results and Discussion

Synthesis and Characterization

The design of the bifunctional catalyst was influenced by Takemoto's discovery that the organocatalyst reported in Figure 1 effectively promoted the conjugate addition of diethyl malonate to nitrostyrene.[9] The catalysis was believed to involve deprotonation of malonate by the tertiary amino group and activation of the nitroalkene by formation of a double H-bond between the relatively acidic protons of the thiourea moiety and the nitro group.[10]

On these bases, the three bi-functional catalysts **1–3** reported in Figure 1 were synthesized by the co-condensation method.[3,7] We reasoned that the two functional groups, the tertiary amine and the thiourea moiety, could be forced in proximity by the silica scaffold and could co-operate by simultaneous activation of a nucleophile and an electrophile, like in Takemoto's catalyst. In principle, this approach allows an easy preparation of a multifunctional heterogeneous recoverable and reusable catalyst, by simple assembly of different precursors.

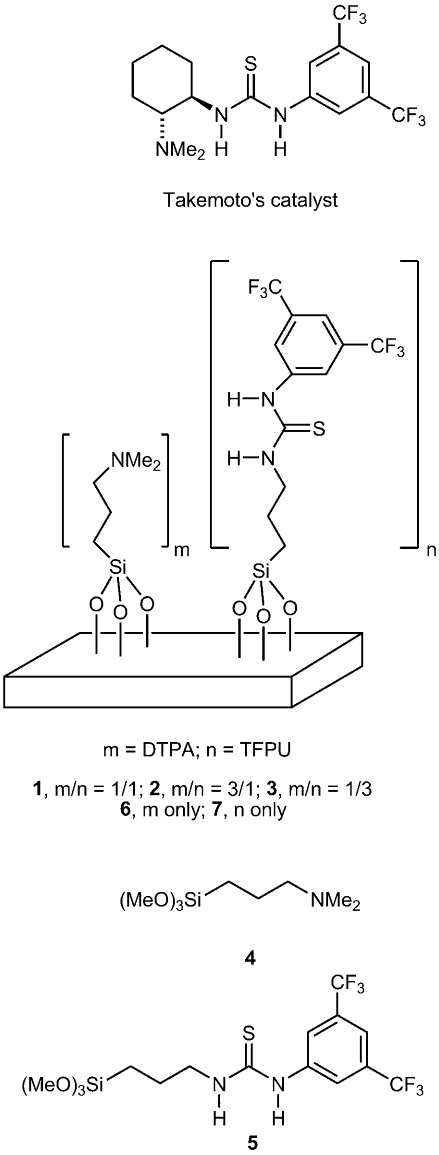


Figure 1. Structures of Takemoto's catalyst, bifunctional catalysts **1–3**, their precursors **4** and **5**, and monofunctional species **6** and **7**.

Catalysts **1–3** are identified by the initial molar ratio of their trialkoxyorganosilane precursors, namely *N*,*N*-dimethyl-3-trimethoxysilylpropanamine (DTPA, **4**) and *N*-(3,5-bistrifluoromethylphenyl)-*N*′-(3-trimethoxysilyl-1-propyl)thiourea (TFPU, **5**). Compound **4** is commercially available as are 3-trimethoxysilylpropanamine and 3,5-bis(trifluoromethylphenyl) isothiocyanate required for the preparation of compound **5**. Monofunctional catalysts **6** and **7** were also prepared by the same approach.

The actual concentrations of the DTPA and TFPU functional groups were determined by the previously described solid-state ^{13}C cross-polarized magic angle spinning (CP MAS) and ^{29}Si MAS NMR spectroscopic methods.[7] The total surface concentrations of the organic residues (DTPA + TFPU) in catalysts **1–3** were determined to be 1.52, 1.44, and 1.16 $mmol\,g^{-1}$, respectively. The DTPA/TFPU concentration ratios for **1–3** were 53/47, 68/32, and 22/78, respectively, in fair agreement with the stoichiometric ratios of the trialkoxyorganosilanes employed for their synthesis.

The structural properties of catalysts **1–3** were investigated using different techniques. Powder XRD patterns revealed the complete amorphous character of these materials. This was expected because of the very rapid gelation of the mixture containing the precursors of the final products in the synthesis of the materials. The XRD patterns of catalysts **1–3** were dominated by a very broad band in the 15–25° 2θ interval, diagnostic of the presence of disordered silica (see Supporting Information). Amorphous functionalized silicas are among the most widely studied and used organic-inorganic hybrid solids for catalytic applications.[2c]

Morphological examination of the sample particles was performed by collecting images of the surfaces by SEM analysis. The images of the surfaces of all the inorganic-organic hybrid materials compared with those of bare silica display a variety of particle shapes and sizes. Figure 2 shows the micrographs of **1**, chosen as an example, at two different magnifications. Rod-shaped particles of different lengths and diameters (*ca.* 1 μm in length and 500 nm in diameter) with curved hexagonal-shaped tubular morphology quite completely cover irregular polyhedral-shaped grains, associated with the silica morphology.

The presence of the surfactant (cetyltrimethylammonium bromide), employed as templating agent for fabrication of the silica material, directed the formation of an ordered pore structure. The surface areas, pore volumes, and pore size distributions of catalysts **1–3** were determined by N_2 adsorption-desorption isotherms. All surfaces exhibited characteristic type IV BET isotherms consistent with the presence of cylindrical *meso*-scale pores. The step corresponding to capillary condensation in the mesopores appeared in the relative pressures range 0.20–0.35 (Figure 3). A not unique pore population can be detected for the three catalysts; a major population centered at *ca.* 20 Å and a minor one, with larger pore size and broader resolution, at *ca.* 40 Å. In agreement with the literature studies on similar materials,[3a,7] and by comparison with the bare silica (obtained by the same synthetic route), it could be assumed that the functionalized silica materials present a hierarchy of pores; the major population is associated with smaller and well defined mesopores and the minor population with wider pore population, mainly housing the organic functionalities.

The BET surface areas (S.A.) of **1**, **2**, and **3** are of 658, 712, and 772 $m^2 g^{-1}$, respectively. The observed differences could be ascribed to the different DTPA/TFPU concentration ratios of the functional groups (53/47, 68/32, and 22/78 for **1**, **2**, and **3**, respectively).

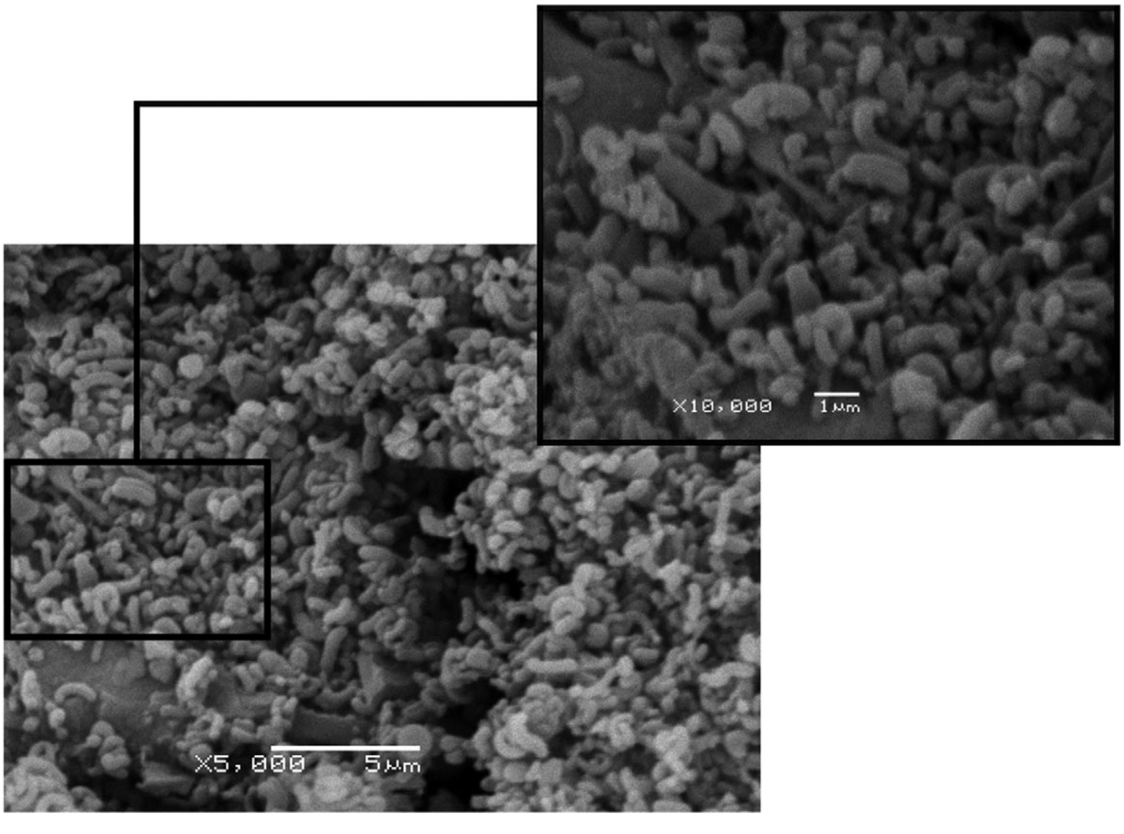


Figure 2. SEM iamges of a sample of bi-functional catalyst **1** at two different magnifications of 5,000× and 10,000×.

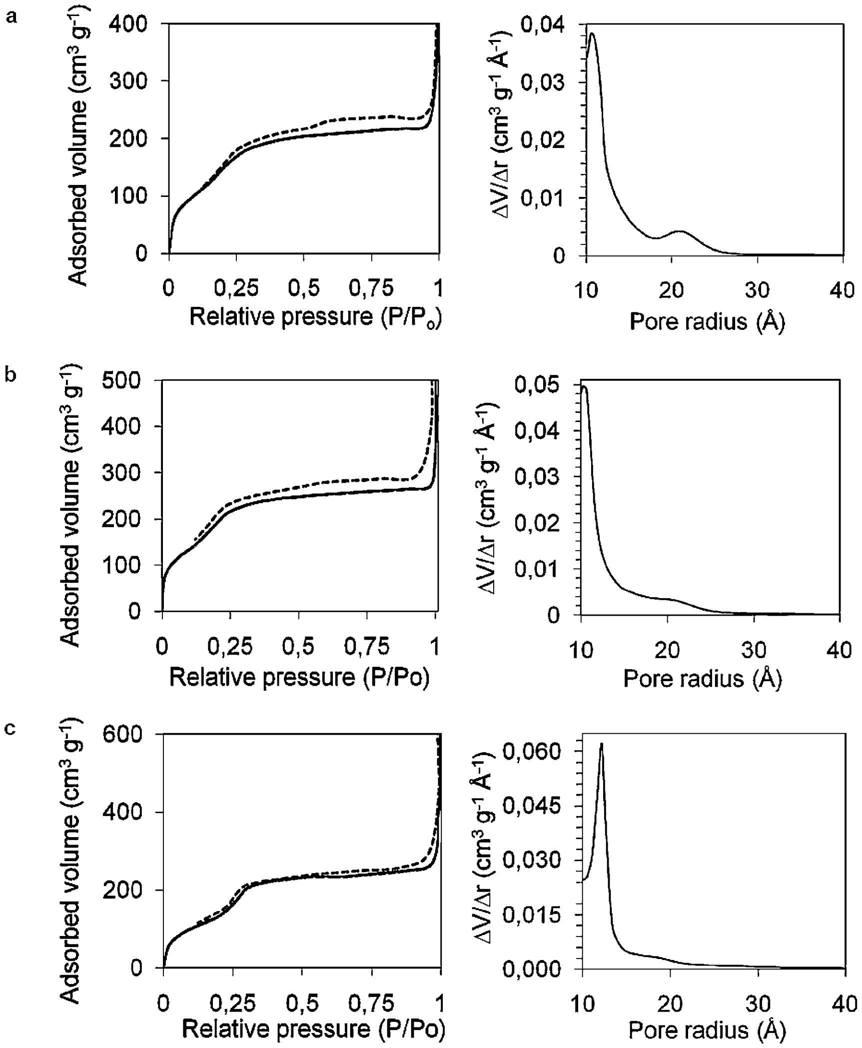


Figure 3. N_2-adsorption-desorption isotherms of the bifunctional catalysts: **a)** **1**; **b)** **3**; and **c)** **2** (*left*) with corresponding pore size BJH distribution curves (*right*).

Table 1. Main morphological properties of the bifunctional catalysts.

Catalyst	N_2 uptake [$cm^3 g^{-1}$ (STP)]	S.A. (BET) [$m^2 g^{-1}$]	Pore volume [$cm^3 g^{-1}$]	Pore size[a] [Å]
1	151	658	0.344	22 (42)
2	163	712	0.594	24 (37)
3	177	772	0.420	21 (42)

[a] Pore size of major and (minor) population.

Because of the modest porosity offered by the three catalysts (Table 1, 4th column), the measured high surface area values should be mainly due to the small siliceous particles.

Further characterization of these hybrid materials was obtained by Fourier transform infrared (FT-IR) spectroscopy. This technique was used both to assess the presence of the functional groups on the surface of the nanoparticles and to determine their relative concentration.[11] Comparison of the FTIR spectra (Figure 4) of bifunctional catalyst **1** and monofunctional material **7**, both containing the thiourea residue, (Figure 1) allowed us to assign the signal at 1555 cm^{-1} to the C=S double bond stretching of this group, the signal at 1388 cm^{-1} to the Ar–N bond stretching, and the signal at 1282 cm^{-1} to the C–F bond stretching; together with other signals at 847, 700, and 682 cm^{-1} the latter signal was considered diagnostic of the *meta* substitution pattern on the aromatic ring. As expected, all of these signals were absent in the spectrum of the dimethylamino-functionalized material **6** (Figure 1). Due to the lack of functional groups providing significant IR signals in compound **6**, comparison of the spectra of the latter with those of compounds **1** and **7** was carried out using a "five points" second derivative function

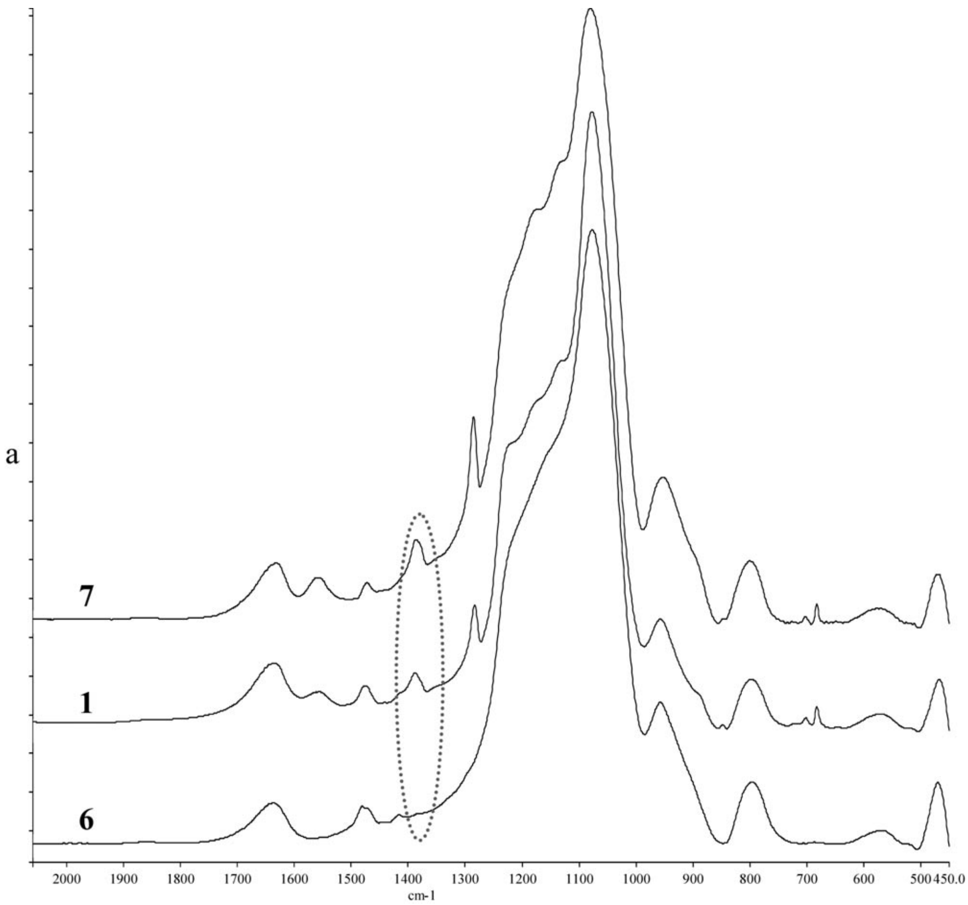


Figure 4. Comparison between the FT-IR spectra of monofunctional (**6**,**7**) and of bifunctional (**1**) materials.

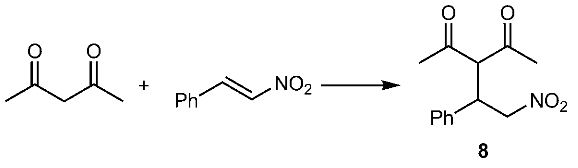
(Figure 5),[12] with the aim of emphasizing differences between the spectra. By this comparison it was possible to demonstrate that materials **1** and **6** shared signals at 1482 and 1418 cm^{-1}, which did not appear in **7**, and that hence can be ascribable to the dimethylamino residue.

It is also interesting to note how the second derivative spectrum of bifunctional catalyst **1** showed the combination of the signals at 1482 and 1474 cm^{-1}, individually present in the spectrum of mono-functional **6** and **7**, respectively.

Remarkably, the FT-IR spectra of bifunctional **1–3** showed relative signal intensities in agreement with the different loading of functional groups (Figure 6, a, 1900–1250 cm^{-1} region; Figure 6, b 1000–650 cm^{-1} region). For instance, with respect to what observed in the spectrum of catalyst **1** (DTPA:TFPU ratio 53:47) the signals at 1282 cm^{-1} (due to C−F bond stretching) and at 1555 cm^{-1} (C=S stretching) increased in the spectrum of catalyst **3** (DTPA:TFPU ratio 22:78) and decreased in that of **2** (DTPA:TFPU ratio 68:32). Accordingly, the signal at 1417 cm^{-1} (assigned to the residue of DTPA, see above) was stronger in the spectrum of compound **2** and weaker in that of **3** (Figure 6, a). The increased intensity of the signals at 847, 700, 682 cm^{-1}, assigned to the $(CF_3)_2$Ar-N part of the thiourea residue, observed on passing from **2** to **1** to **3**, was also evident (Figure 6, b).[13]

Catalytic Activity

To determine whether the bifunctional catalysts **1–3** could act through co-operative catalysis, they were employed in the conjugate addition of acetylacetone to 2-nitrostyrene to afford 3-[1-(1-phenyl-2-nitroethyl)]-2,4-pentanedione **8** [Eq. (1)].[14] It must be noted that conjugate addition reactions have never before been reported for organic catalysts supported on mesoporous silica nanoparticles.[15]



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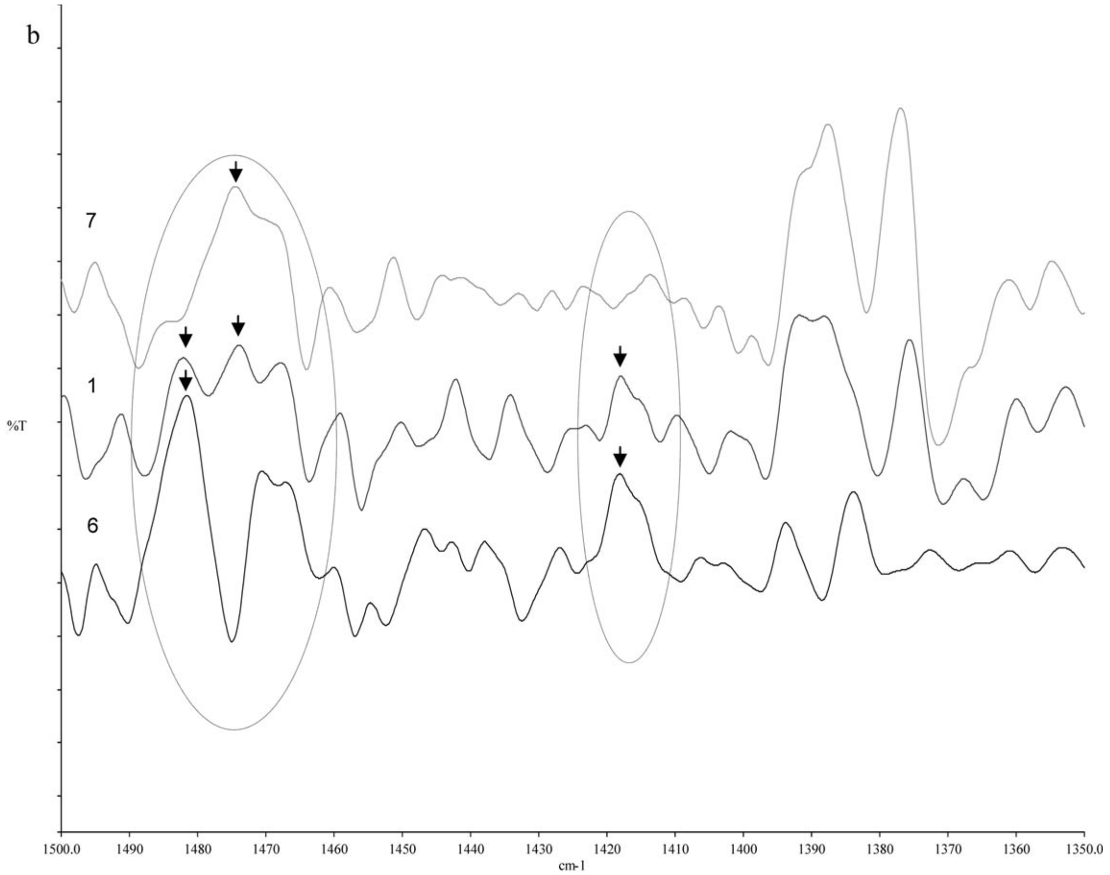


Figure 5. Second derivative (five points) spectra of materials **1**, **6**, and **7**.

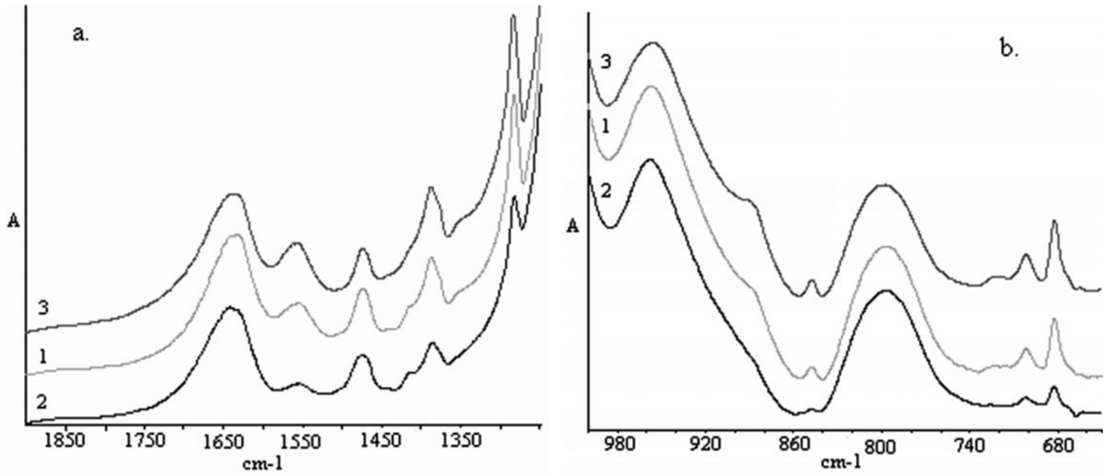
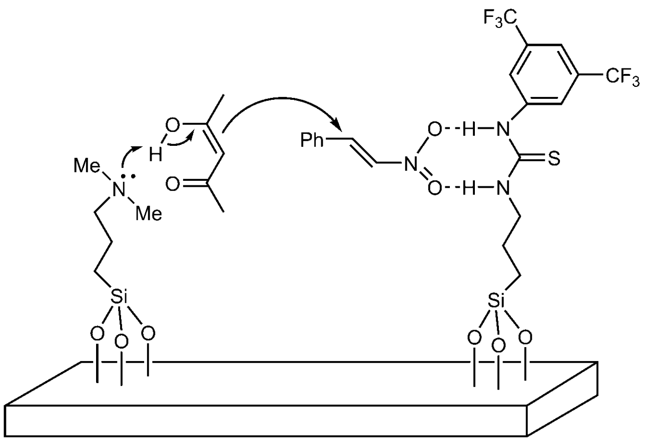


Figure 6. Comparison between FT-IR spectra of compounda **1–3** (**a** 1900–1250 cm^{-1} region; **b** 1000–650 cm^{-1} region).

As mentioned before, we believed that the tertiary amine and thiourea groups could act co-operatively on the nucleophile donor and on the electrophile acceptor, respectively, facilitating the process, as depicted in Scheme 1. The results obtained by studying the reaction of Eq. (1) (1.6 mol equiv. of acetylacetone, 1.0 mol equiv. of 2-nitrostyrene, diethyl ether, room temperature, 24 h) carried out in the presence of 10 mol% of the catalyst (based on the total surface concentrations of the organic residues)[16] were consistent with this hypothesis.

As can be seen from the data reported in Table 2, bifunctional catalyst **1**, featuring a 53/47 loading of basic and acid sites, promoted the reaction in 80%



Scheme 1. Co-operative activation of nucleophile donor and electrophile acceptor by bifunctional catalyst **1–3**.

Table 2. Synthesis of adduct **8** in the presence of different catalyst species.

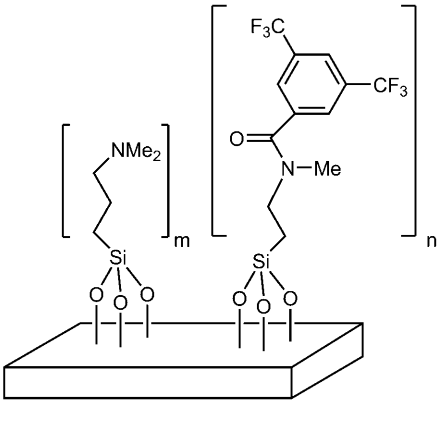
Entry	Catalyst	Amine/thiourea ratio	Yield [%]
1	**1**	53/47	80
2	**2**	68/32	54
3	**3**	22/78	56
4	**4**	1/0	25
5	**6**	1/0	43
6	**5**	0/1	0
7	**7**	0/1	0
8	**4+7**	1/1	71
9	TEA+**7**	1/1	75
10	**6+7**	1/1	53
11	**4+5**	1/1	82

yield (entry 1). Varying the ratios of the supported tertiary amine and thiourea functions to 68/32 or 22/78, as in catalysts **2** and **3**, respectively, led to lower yields (*ca.* 55%, entries 2 and 3). In this respect, the behaviour of our catalysts differed from that of Lin's[7] and Davis' catalysts,[8a] for which the best catalytic activity was observed with unbalanced mixtures of active sites.

In the presence of either non-supported (entry 4) or supported (entry 5) tertiary amine catalysts **4** and **6** the reaction proceeded in lower yields (25 and 43%, respectively), an indication of the active role played by the thiourea group in the catalytic process. The better yield observed with the supported catalyst **6** instead of non-supported **4** could suggest that also the relatively acidic silanol protons present on the surface of the support can activate to some extent the nitroalkene.[6a–d] However, the fact that when a thiourea residue is present on the catalysts better yields are obtained (entries 1–3), indicates that this residue is a stronger activator than the silanol groups.

As expected on the basis of the proposed activation mechanism, catalysts containing only a thiourea group such as **5** and **7** were not effective (entry 6 and 7). However, when the supported monofunctional thiourea material **7** was used in combination with non-supported tertiary amine **4** (entry 8) or with triethylamine (TEA, entry 9) good yields were obtained (71 and 75%, respectively). These were higher than those observed in the presence of only tertiary amines (entries 4 and 5), a fact that again points to an active role for the thiourea residue. Interestingly, a physical mixture of equimolar amounts of the monofunctional derivatives **6** and **7** was less effective than the bifunctional catalyst **1** (entry 10), showing that the proximity of the two active sites on the surface, a peculiar feature of the bifunctional catalyst, pays off in terms of co-operativity. Remarkably, the activity of bifunctional **1** can be replicated only by operating under homogeneous reaction conditions with an equimolar mixture of **4** and **5** (entry 11).

With the aim of further demonstrating the true co-operativity between tertiary amine and thiourea residues in our bifunctional catalysts, it was decided to check whether the observed enhancement in the yield of adduct **8** observed on passing from the supported tertiary amine catalyst **6** (entry 5) to the bifunctional catalysts **1–3** (entries 1–3) was not due to a more favourable modulation of surface properties induced by the thiourea residue.[1,6,7] In principle, it could be hypothesized that the thiourea residue, for instance by creating a lipophilic environment around the tertiary amine site,[6e] makes this site more accessible to the hydrophobic reagents of Eq. (1) and thus enhances the yield of this reaction. With this goal in mind, the bifunctional material **9** (Figure 7), featuring a stoichiometric 1/1 ratio of the tertiary amine residue and of a tertiary amide group structurally related to the thiourea moiety of **1–3**, was synthesized and tested as



9, m/n = 1/1

Figure 7. Structure of bifunctional material **9**.

catalyst in the reaction of Eq. (1) under the conditions of entry 1, Table 2.

We were pleased to find that, from this reaction, adduct **8** was isolated in 43% yield, a value identical to that observed in the reaction promoted by the monofunctionalized amine catalyst **6**. We believe that together with the previous findings (Table 2), this result could be taken as a strong indication of co-operativity for bifunctional catalysts **1**–**3**.

The effect of the solvent on the efficiency of the reaction was then investigated in the case of bifunctional catalyst **1**. The results (Table 3) showed that the use of dichloromethane allowed us to obtain the same yield observed in diethyl ether (80%), while other solvents were less effective. However, when the reaction was carried out in the absence of solvent a quantitative yield was observed. Furthermore, it was shown that, under these conditions, the reaction time could be drastically reduced from 24 to 3 h.

Table 3. Synthesis of adduct **8** in the presence of catalyst **1** in different solvents.

Solvent	Time [h]	Yield [%]
Et_2O	24	80
CH_2Cl_2	24	80
Toluene	24	56
MeCN	24	45
DME	24	30
Dioxane	24	10
Neat	24	100
Neat	3	100
Neat	1	68

We next demonstrated that the catalyst really operates under heterogeneous conditions. A mixture of acetylacetone, 2-nitrostyrene, and catalyst **1** (10 mol%) was stirred at room temperature until a yield of 35% was obtained, as monitored by NMR analysis. The mixture was then diluted with diethyl ether, the catalyst was filtered off and the volatile materials were evaporated. To the obtained residue, containing 2-nitrostyrene and product **8**, acetylacetone was added to restore the initial reagent ratio, and the mixture was allowed to stir at room temperature for additional 18 h. ^{1}H NMR analysis showed no further formation of product **8**. This result showed that the catalysis was indeed heterogeneous and that the siliceous material did not suffer from any leaching of catalytically active organic residues into the reaction environment.

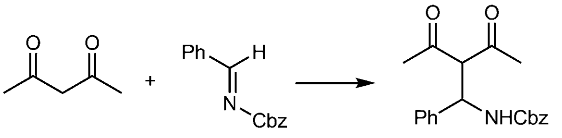
The excellent results obtained in the absence of solvent led us to preliminarily investigate the issue of recyclability of catalyst **1** since recovery and recycling is the major goal of catalyst supporting.[5] After a first reaction was performed for three hours at room temperature without solvent in the presence of 10 mol% of the catalyst (entry 1, Table 4), the reaction mixture was simply rinsed with diethyl ether (100 mL/30 mg of catalyst), and the catalyst was recovered by filtration, dried under vacuum under different conditions (see Table 4), and recycled. The results are collected in Table 4.

Table 4. Recycling experiments with catalyst **1**.

Entry	Catalyst regeneration conditions	Cycles	Time [h]	Yield [%]
1		1	3	100
2	Vacuum, 4 h at 25 °C	2	24	75
3	Vacuum, 4 h at 25 °C	3	24	55
4	Vacuum, 4 h at 90 °C	2	24	100
5	Vacuum, 4 h at 90 °C	3	24	67
6	Vacuum, 4 h at 150 °C	2	3	100
7	Vacuum, 4 h at 150 °C	3	3	93
8	Vacuum, 4 h at 150 °C	4	3	91

These data showed that the catalyst regeneration procedure played a fundamental role in determining the activity of the recovered material. After drying the catalyst under vacuum at 25 °C for 4 h, a yellow powder was recovered, whereas a freshly prepared catalyst sample was perfectly white.[17] When employed in a second reaction (entry 2, Table 4) this recovered material showed to be less active, affording the product in 75% yield after 24 h (first cycle: 100% yield after 3 h, entry 1, Table 4). The catalyst activity further decreased in a third cycle (entry 3). By regeneration of the catalyst at higher temperature (4 h under vacuum at 90 °C) better results were obtained in the second reaction (100% yield after 24 h, entry 4) but once again a decrease in the yield was observed in the third cycle (67% yield, entry 5). Finally reliable catalyst regeneration conditions were identified; by drying the recovered catalyst under vacuum at 150 °C for 4 h[18] its activity was preserved and also in a second cycle the product was obtained in 100% yield in just 3 h reaction time (entry 6).[19] The yield still remained very high (93% and 91%) in a third and fourth cycle, clearly assessing the recyclability of the properly regenerated catalyst **1** (entries 7 and 8).

Finally, the use of catalyst **1** in another reaction was investigated. On the basis of the recognized ability of thiourea-based organocatalysts to activate *N*-carboxyalkylimines toward nucleophilic attack,[9b] the *N*-carbobenzyloxy (Cbz) imine of benzaldehyde was reacted with acetylacetone in the presence of 10 mol%[16] of catalyst **1** in toluene at room temperature for 18 h to afford product **10** in 83% isolated yield [Eq. (2)].[20]



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Conclusions

In conclusion, mesoporous silica nanoparticles carrying different loadings of tertiary amine and thiourea residues (residues ratios 53/47, 68/32, and 22/78, respectively) were synthesized by the co-condensation methods and fully characterized by CP MAS NMR, powder XRD, SEM, BET, BJH and FT-IR techniques. These materials were tested as bifunctional catalysts in the conjugate addition of acetylacetone to 2-nitrostyrene, a reaction that under solvent-free conditions occurred in quantitative yield. By carrying out several experiments with the bifunctional catalysts featuring different molar ratios of active sites, and with different combinations of monofunctional supported and non-supported catalyst, the co-operativity of the tertiary amine and thiourea residues in catalyzing the reaction was demonstrated. The use of the bifunctional catalyst was extended to the addition of acetylacetone to *N*-Cbz-benzaldimine. Catalyst recycling for a total of three reaction cycles was also demonstrated. Work is in progress toward the synthesis of bifunctional materials featuring enantiomerically pure organocatalysts in order to exploit catalyst co-operativity in the context of stereoselective synthesis.

Experimental Section

General

All commercially available reagents including dry solvents were used as received. Organic extracts were dried over sodium sulfate, filtered, and concentrated under vacuum using a rotatory evaporator. Non-volatile materials were dried under high vacuum. Reactions were monitored by thin-layer chromatography on pre-coated Merck silica gel 60 F254 plates and visualized either by UV or by staining with a solution of cerium sulfate (1 g) and ammonium heptamolybdate tetrahydrate (27 g) in water (469 mL) and concentrated sulfuric acid (31 mL). Flash chromatography was performed on Fluka silica gel 60.

NMR Spectroscopy

Solid state NMR spectra were obtained at 125.62 (^{13}C) and at 99.36 (^{29}Si) MHz on a Bruker Avance 500 spectrometer, equipped with a 4 mm magic angle spinning (MAS) broadband probe (spinning rate ν_R up to 15 kHz). The MAS spectra were recorded on solid samples, (typically 0.15 g); each sample was packed into a 4 mm MAS rotor (50 µL sample volume) spinning at 13 kHz and at a temperature of 330 K. Direct polarization (DP) and variable amplitude cross polarization (CP) methods were used for ^{29}Si and ^{13}C, respectively. 250 scans and a delay of 300.0 s have been used for the acquisition of ^{29}Si NMR spectra, and 10,000 scans and a delay of 2.0 s for that of ^{13}C NMR spectra. These measurements provided quantitative evidence for functionalization of the materials with the organic moieties and confirmed their structure. The assignments of ^{29}Si resonances followed Lin's report;[7] the assignments of ^{13}C resonances were based on comparison with the corresponding unbound compounds. The spectra are reported in the Supporting Information. From these spectra T^2, T^3, Q^2, Q^3, and Q^4 values were obtained. These data are collected in Table 5.

N_2 Physisorption

Surface area and porosity were determined by collecting N_2 adsorption/desorption isotherms at −196 °C using a Carlo Erba Sorptomatic 1900 series instrument. Prior to the analysis, the samples (*ca.* 0.1 g) were outgassed at 90 °C for 3 h, after this temperature remained constant. Specific surface area was calculated *via* the BET model at relative pressure of $P/P_o = 0.05$–0.35, assuming the molecular N_2 diameter in the adsorbed state as 16 Å^2. The total pore volume was estimated from the uptake of nitrogen at a relative pressure of $P/P_o = 0.99$. Pore size distribution was obtained from the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) model equation.[21]

Scanning Electron Microscopy

Scanning electron micrographs (SEM) were obtained by a JEOL JSM-5500 LV operating at 20 kV.

Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectroscopy was used to determine the vibrational frequencies of surface functional groups.[11] Spectra were acquired on a Spectrum One FTIR Spectrophotometer

Table 5. Relative concentrations of T^n and Q^n silicon groups (in %), surface coverage (*SC*, in %), molecular concentrations of organic functionalities (*MC*, in mmol g^{-1}), molecular formulas (*MF*), DTPA:TFPU molar ratios (*MR*), and DTPA/TFPU concentrations (in mmol g^{-1}) derived from solid state ^{13}C CP MAS- and ^{29}Si MAS-NMR data.

Catalyst	T^2	T^3	Q^2	Q^3	Q^4	*SC*	*MC*	*MF*[a]	*MR*	Concentration
1	6	8	6	37	43	25	1.52	$(SiO_2)_{100}(H_2O)_{21}(ORG)_{14}$	53:47	0.80/0.72
2	5	7	6	35	47	23	1.44	$(SiO_2)_{100}(H_2O)_{20}(ORG)_{12}$	68:32	0.98/0.46
3	4	7	6	40	43	19	1.16	$(SiO_2)_{100}(H_2O)_{22}(ORG)_{11}$	22:78	0.26/0.90

[a] ORG indicates the organic functional groups. For the definitions of T^2, T^3, Q^2, Q^3, and Q^4 see refs.[3a,7]

(Perkin–Elmer) in the range 4000–450 cm^{-1} (transmittance mode). FT-IR grade KBr was ground for 5 min and dried at 125 °C. KBr was then mixed with silicate in an agate mortar for 1 min at 0.33% (w/w) concentration. Spectra were recorded selecting a scan number of 300 and 4 cm^{-1} resolution. The background of pure KBr was separately recorded using the same conditions and automatically subtracted from sample spectra.

Synthesis of the Catalysts

The procedure reported by Lin et al.[7] was followed. The preparation of catalyst **1** is representative of the procedure. A solution of cetyltrimethylammonium bromide (365 mg, 1 mmol) in water (88 mL) and 2 M NaOH (1.3 mL) was mechanically stirred at 550 rpm at 80 °C for 30 min. The stirring speed was decreased to 200 rpm and tetraethoxysilane (TEOS, 1.82 mL, 8.16 mmol), compound **4** (0.121 mL, 0.525 mmol), and compound **5** (237 mg, 0.525 mmol; see the Supporting Information for its synthesis) were rapidly added in this order. After 2 min stirring at 200 rpm a precipitate was formed. Stirring at 500–600 rpm was continued for 2.0 h at 80 °C and the mixture was filtered while still hot. The solid was washed with water (150 mL) and MeOH (150 mL), and dried under high vacuum for 3 h to afford a white material (794 mg). This was then treated with a solution of concentrated HCl (0.6 mL) in MeOH (80 mL) under mechanical stirring for 2.5 h at 60 °C in order to remove the surfactant. The cooled mixture was filtered and the solid washed again with water and MeOH (100 mL each). The white solid was dried under high vacuum for 3 h at 90 °C, to afford a final yield of 576 mg of compound **1**. Other supported catalysts were prepared by identical procedures in similar yields. See text for their characterization.

Synthesis of 3-[1-(1-Phenyl-2-nitroethyl)]-2,4-pentanedione (8)

To a homogeneous mixture of 2-nitrostyrene (64 mg, 0.43 mmol) and acetylacetone (0.070 mL, 0.68 mmol), catalyst **1** (28 mg, 10 mol%) was added and the mixture was magnetically stirred at room temperature for 3 h. Diethyl ether (10 mL) was then added and the suspension was filtered under vacuum on a Durapore ® 0.1 μm membrane filter (Millipore). The catalyst was washed with diethyl ether (total volume 100 mL), dried under vacuum at 90 °C, and recovered in $>90\%$ yield. The filtrate was concentrated under vacuum to afford the product; yield: 107 mg (100%). This was identical by ^{1}H NMR to an authentic sample of compound **8**.[14]

Synthesis of 3-[*N*-(Carbobenzyloxy)aminophenylmethyl]-2,4-pentanedione (10)

To a solution of *N*-carbobenzyloxybenzaldimine (36 mg, 0.15 mmol) and acetylacetone (0.031 mL, 0.30 mmol) in dry toluene (2 mL) catalyst **1** (10 mg, 10 mol%) was added and the mixture was stirred at room temperature for 18 h. The reaction was then worked up as described above to afford the product after purification by flash chromatography with a 9:1 and then 7:3 hexanes:ethyl acetate mixture as eluants; yield: 43 mg (83% yield). The product was identical by ^{1}H NMR to an authentic sample of compound **10**.[20]

Supporting Information

Powder XRD determination of material **1**; synthesis of thiourea **5**; NMR spectra of bifunctional catalysts are available as Supporting Information.

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