Chapter 4

THE SYNTHESIS OF MESOPOROUS SILICA FUNCTIONALIZED WITH SULFONIC ACID/PRIMARY AMINE PAIRS

Abstract

Mesoporous silica catalysts functionalized with both sulfonic acid and amine groups have been recently shown to be good catalysts for the aldol reaction of acetone and *p*-nitrobenzaldehyde. In these materials, acid and base groups were randomly-distributed in SBA-15 in a one-pot (direct) synthesis. To investigate the effect of spatial orientation of these acid and base groups, a catalyst was prepared in which sulfonic acid and amine groups are organized into pairs on the surface. This material was synthesized by first grafting onto the surface an organosilane containing a propylsultone ring, which was subsequently reacted with ammonia gas to ring-open the sultone into sulfonic acid and primary amine groups separated by a short three-carbon spacer. The resulting material is found to be completely *inactive* in catalyzing the aldol reaction, because the acid and base groups neutralize each other, while both acid-only and base-only catalysts performed significantly better. Thus the catalytic behavior of randomly-bifunctionalized acid/base catalysts is due to those acid and base groups which are tethered far enough away from each other to avoid neutralization.

Introduction

Acids and bases can be used to catalyze a vast array of different chemical reactions. Greater catalytic activity can sometimes be achieved through a combination of acid and base catalysis, but with homogeneous catalysts, strong acids and bases neutralize each other, destroying the catalytic activity. Weak acids and weak bases can coexist in solution, and there are many reports of homogeneous cooperative catalysis between amine bases and weak acids such as carboxylic or phenolic acids. But rarely can strong acids coexist in solution with even weak bases, unless the two catalysts are designed with structural barriers to provide steric hindrance.[1, 2]

In the case of heterogeneous catalysts, on the other hand, both acid and base groups can coexist in the same solid material. Because the acids and bases are fixed spatially within the solid, they cannot neutralize each other. Acids and bases have been immobilized on two separate supports to provide two-step catalytic sequences[1, 3-6]. In these cases, the acid and base are spatially isolated from one another, and cooperative catalysis is impossible. In a recent report by Zeidan et al.,[7] arylsulfonic acids and amine bases were incorporated into mesoporous silica (SBA-15) in a one-pot synthesis and the resulting acid-base catalyst exhibited cooperative catalysis, in which the acid and base groups both contributed to the catalytic activity in the aldol reaction between acetone and *p*-nitrobenzaldehde. The acid groups could be selectively poisoned by the addition of homogeneous base, leading to reduced activity, and the base groups could be similarly poisoned by homogeneous acid, confirming the bifunctional nature of the catalyst.

We sought to investigate how the spatial positioning between the sulfonic acid and primary amine groups affect the cooperative catalytic activity. If the acid and base groups are too far apart (*e.g.*, immobilized on two different supports) then cooperativity is impossible. Thus one would expect that acid sites in proximity to base sites are responsible for the enhanced activity of the bifunctional catalysts. But is the activity of randomly-bifunctionalized sulfonic acid/primary amine catalysts due primarily to acid and base sites tethered far enough away from one another that they cannot neutralize, or to acid and base sites in very close proximity that can directly interact with one another? To distinguish between these possibilities (see Figure 4.1), we designed a silica catalyst bearing pairs of sulfonic acid and primary amine groups. If the activity of the randomly-bifunctionalized catalyst is due to closely interacting acid/base sites, then one would expect the acid/base paired catalyst to exhibit even greater catalytic performance, because every acid site is paired to a base site. If, on the other hand, the activity of the random acid/base catalysts is due to acid and base groups that are too far apart to neutralize, then the acid/base paired catalyst should be inactive.

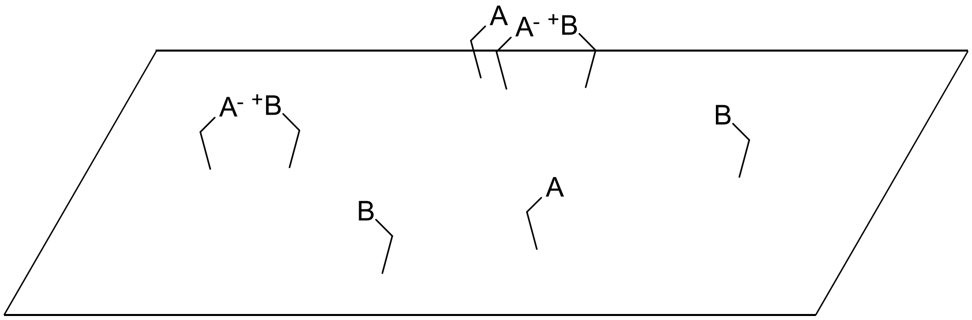

Figure 4.1. Schematic representation of a catalyst surface functionalized with covalently tethered, randomly-distributed acid (A) and base (B) groups. Some of these groups will be spatially isolated and unable to exchange protons, while others will be close enough to interact directly with another nearby group, allowing proton exchange and equilibration with the ion-pair form (represented by A^-/B^+ pairs).

Results and Discussion

Silica catalysts containing sulfonic acid and primary amine pairs were prepared according to Scheme 4.1. First the sultone-containing silane **1** was grafted onto the surface of SBA-15 to form **SBA-g1** (see Chapter 2). The loading of this material was estimated by thermogravimetric analysis (TGA) to be 0.35 mmol/g.* The surface-bound sultone groups were ring-opened by reaction with gaseous ammonia, a reaction that proceeds readily at room temperature[8] to produce a sulfonic acid and a primary amine separated by a three-carbon spacer.

Initially, the basic ammonia atmosphere leads to ammonium sulfonate species that must be acidified to remove the ammonium counterions. In a procedure analogous to the synthesis procedure of Zeidan et al.[7] (in which the materials were synthesized in strongly acidic solution and then neutralized), the paired acid/base catalyst was first fully acidified with 0.5 N aqueous HCl, followed by repeated washing with water to neutralize the protonated amines. It is expected that the three-carbon linker is flexible enough that the acid and base can equilibrate between the ammonium sulfonate and free acid/base states. This material is denoted **SBA-ab-p** (acid/base pairs).

The ring-opening reaction was monitored by ^{13}C CP/MAS NMR. After one day of reaction with gaseous ammonia, the peak at 67 ppm has disappeared, indicating that the ring-opening reaction is complete (see Figure 4.2). The loading of the amine and amine/acid material was estimated by TGA to be ~ 0.38 mmol/g, comparable to that of the sultone starting material.

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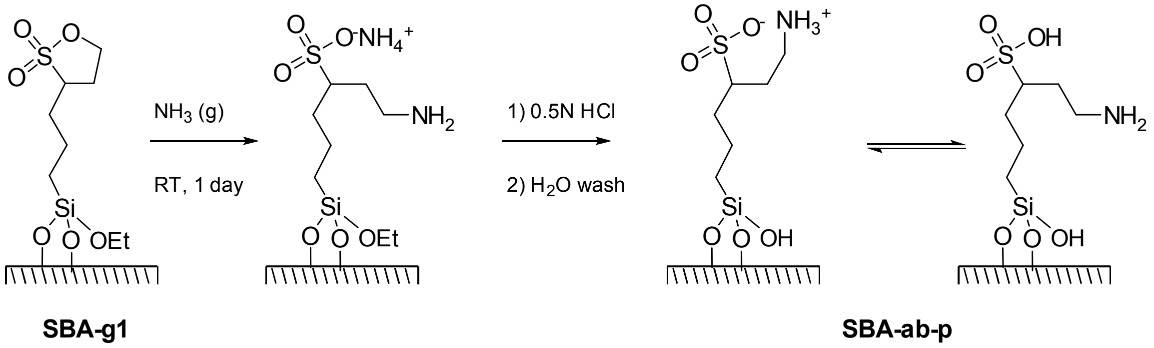
* The mass loss between 200°C and 600°C was attributed to the loss of the organic groups.



Scheme 4.1. Ring-opening and subsequent acidification and neutralization of sultone-grafted SBA-15, leading to **SBA-ab-p**, containing sulfonic acid/amine pairs

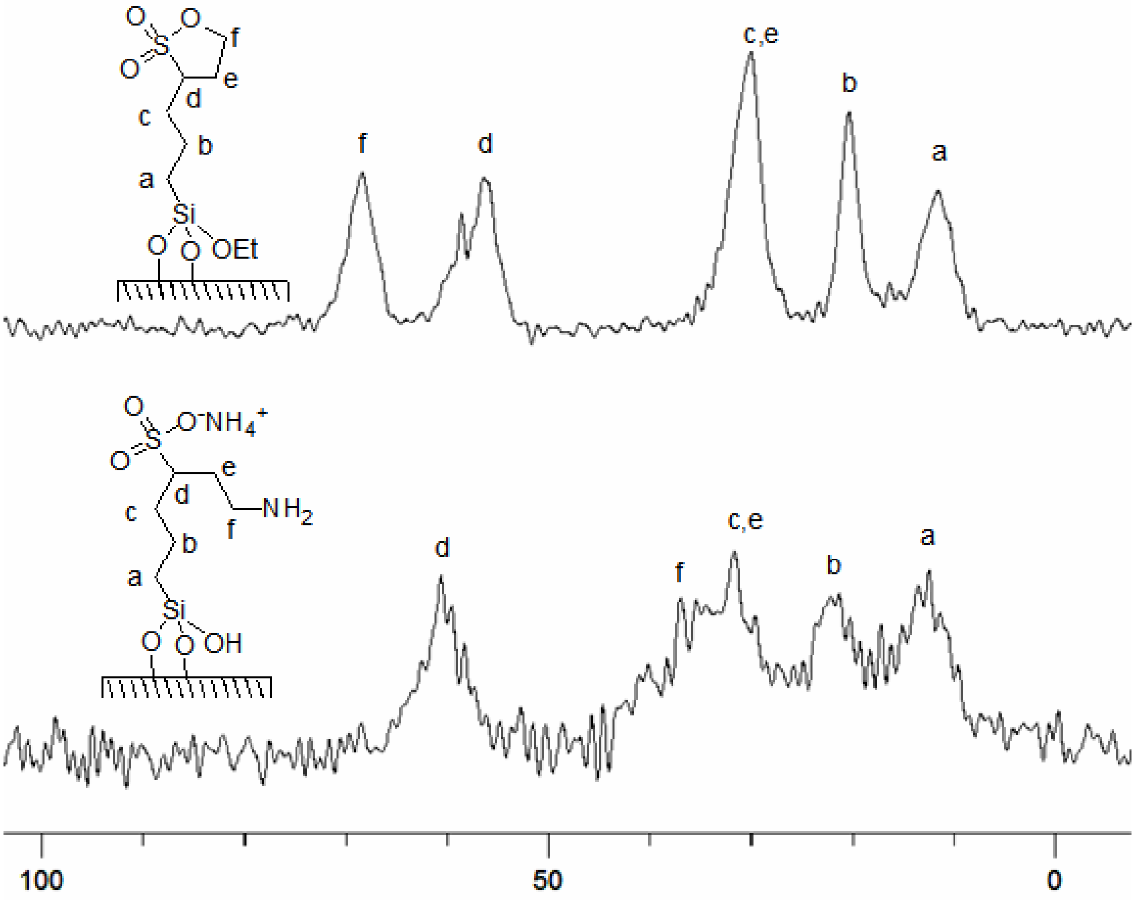
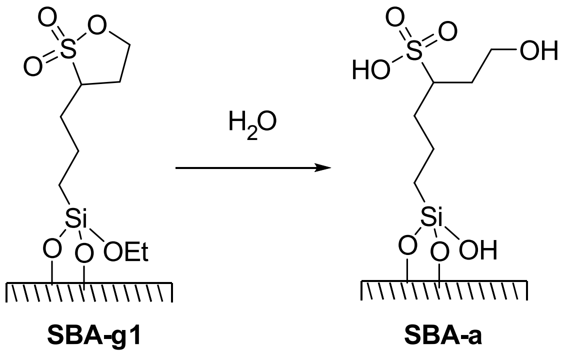


Figure 4.2. ^{13}C CP/MAS NMR spectra of sultone-functionalized **SBA-g1** before (top) and after (bottom) reaction with ammonia to form **SBA-ab-p**

A material containing only sulfonic acid groups was obtained from the same sultone-functionalized silica by hydrolyzing the sultone ring in water, as previously reported[9] (see Scheme 4.2). The resulting material, denoted **SBA-a**, contains sulfonic acid groups but no amines (a pendant hydroxyl group is tethered to the acid). The acid loading of this material was measured by ion-exchange with NaCl, followed by titration with NaOH, and was found to be 0.19 mmol H^+/g.[†] The lower organic loading of this material compared to the starting material (0.3 mmol/g) means that some of the organic groups are lost during the hydrolysis step.

A material containing only base groups (**SBA-b**) was prepared by grafting 3-aminopropyltriethoxysilane onto SBA-15. The amine loading of this material was estimated by TGA to be 0.6 mmol/g.



Scheme 4.2. Hydrolysis of the sultone groups of **SBA-g1** leads to **SBA-a**, containing sulfonic acid groups but no amines

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[†] This ion-exchange/titration method cannot be used to quantify the loading of **SBA-ab-p**; with this material only a very small amount of titratable acid is generated after ion-exchange. This is due to the neutralization of any HCl formed during ion-exchange by the surface amine groups.

Catalytic Reactions

The acid, base, and acid/base-paired catalysts were used in the aldol reaction of acetone and *p*-nitrobenzaldehyde at 50°C. The results are shown in Table 4.1, along with the previously reported results from Zeidan et al.[7] The previously reported catalysts were generated in a one-pot synthesis with amine and/or arylsulfonyl chloride-containing organosilanes, leading to primary amine and arylsulfonic acid sites (which are substantially stronger than alkylsulfonic acids). These catalysts are here denoted **SBA-A** (acid), **SBA-B** (base), and **SBA-AB-r** (acid/base random) with capital letters used to distinguish from the grafted catalysts described above. A summary of the six catalysts is shown in Figure 4.3.

In the previously reported data (Table 4.1, Entries 1–3) the arylsulfonic acid-functionalized catalyst exhibits low catalytic activity. The amine base-functionalized catalyst **SBA-B** is substantially better, and the bifunctional material **SBA-AB-r**, containing a random distribution of acid and base sites, is nearly twice as active as **SBA-B**. Furthermore, selective acid- and base-neutralization experiments confirmed the bifunctional nature of the catalysis, in which both acid and base groups play a role.

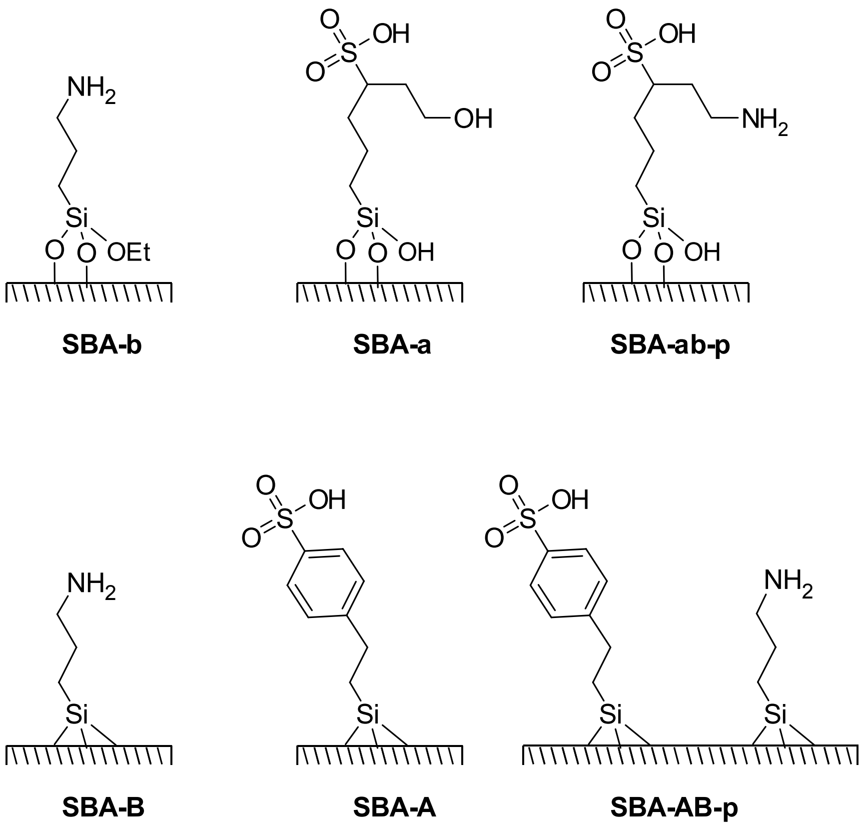
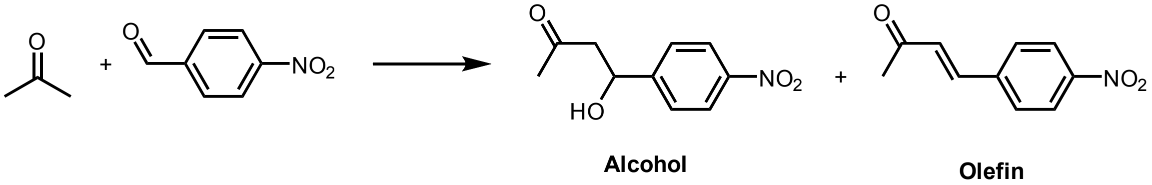


Figure 4.3. Summary of the grafted amine/alkylsulfonic acid SBA-15 catalysts whose synthesis is reported here (top) and the one-pot-synthesized amine/arylsulfonic acid SBA-15 catalysts of Zeidan et al.[7] (bottom)

The catalytic results of **SBA-a** and **SBA-b** are consistent with those of **SBA-A** and **SBA-B**. The acid-only material **SBA-a** exhibits lower activity than **SBA-A**, due to the weaker acid strength, but some catalytic behavior is still present (Entry 4). The amine-grafted **SBA-b** provides 94% yield, compared to only 33% for the one-pot-synthesized **SBA-B**. This difference could be due to the inaccessibility of some of the amine groups in the one-pot-synthesized material, whereas every amine group in the grafted **SBA-b** must be on the surface. It is also likely that the loading of **SBA-B** was overestimated by thermogravimetry due to residual structure-directing agent that is not fully removed during the extraction process (a difficulty not present when silanes are grafted onto calcined silica).

SBA-ab-p, in which the acid and base groups are both present but are arranged into pairs, is catalytically inactive in the aldol reaction (Entry 6). Thus the pairing of the alkylsulfonic acid and amine base allows for complete neutralization of the acid and base sites, leading to a completely inactive catalyst. The high catalytic activity of **SBA-AB-r** must therefore be due to isolated acid and base groups that are too far apart to neutralize one another.



Entry	Catalyst(s)	Sulfonic Acid Type	Loading (mmol/g)[b]	Alcohol Yield	Olefin Yield	Total Yield
1[a]	**SBA-A**	aryl	0.49	8%	8%	16%
2[a]	**SBA-B**	N/A	0.51	25%	8%	33%
3[a]	**SBA-AB-r**	aryl	0.55[c]	45%	17%	62%
4	**SBA-a**	alkyl	0.19	3.1%	0.4%	3.5%
5	**SBA-b**	N/A	0.6	74%	19%	94%
6	**SBA-ab-p**	alkyl	0.3[c]	0.1%	0.0%	0.1%

Table 4.1. Catalytic results of heterogeneous acid/base catalysts in the aldol reaction between acetone and *p*-nitrobenzaldehyde (50 mM aldehyde in acetone, 10 mol% total catalyst [acid + base], 50°C, 20 hr)

[a] Data taken from Ref. 7; catalysts prepared in one-pot synthesis.
[b] All loadings estimated by TGA except for **SBA-a**, measured by titration.
[c] In the case of bifunctional materials, loading refers to each functional group.

Conclusions

A mesoporous silica material featuring alkylsulfonic acid and primary amine groups arranged into pairs was successfully synthesized. The aldol catalytic activity of this acid/base-paired material was very low, compared to the sulfonic acid or amine alone. This result provides insight into the mechanism of randomly-distributed acid/base catalysts such as **SBA-AB-r**, that contain some isolated acid and base sites in addition to acid sites which are in close proximity to base sites. The proximal acid/base groups neutralize and do not contribute to the overall catalytic activity of the material, which is dominated by those acid and base groups that are isolated enough to avoid neutralization while still in close enough proximity to provide cooperative acid/base catalysis. It is unknown how many of the acid and base groups in **SBA-AB-r** are neutralized and how many are active and responsible for the catalytic behavior of this material, meaning that the true turnover number of the active sites cannot be calculated without further characterization of the acid and base sites on the catalyst.

With the knowledge that the acid and base groups must be sufficiently separated from one another, one can now begin to design materials with acid and base groups positioned into pairs at a greater distance such that they cannot neutralize. For instance, using a molecular precursor containing hydrolyzable sulfonate ester and carbamate bonds to a rigid cleavable linker, one could synthesize a material such as the one shown in Figure 4.4 that could be used to imprint a silica surface with sulfonic acid and amine pairs at a fixed distance sufficient to prevent neutralization.

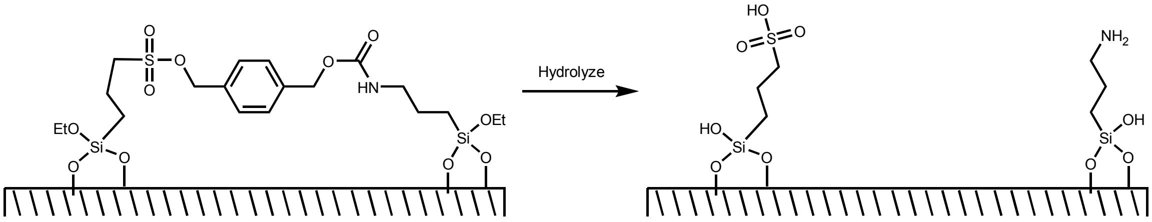


Figure 4.4. Proposed route to sulfonic acid/amine-paired silica in which the acid and base groups are too far apart to neutralize

Experimental

Materials. Toluene was distilled over sodium immediately before use. All other solvents were analytical grade and used as received. Organosilanes were purchased from Gelest. All other chemicals were purchased from Aldrich and used as received. All reactions were performed under an argon atmosphere.

SBA-g1. SBA-15 (1.0 g, synthesized according to the literature procedure[10]) was dried under flowing argon at 170°C for 4 hours. After cooling, dry toluene (50 mL) was added via syringe and the mixture was stirred vigorously to form a uniform suspension. Sultone-containing organosilane **1** (0.7 mmol, synthesized according to the literature procedure[9]) was added dropwise via syringe. The suspension was stirred for 45 minutes at room temperature, then refluxed for 16 hours. After cooling to room temperature, the solids were filtered and washed with toluene and dichloromethane (3 x 20 mL each). The solids were Soxhlet-extracted with dichloromethane overnight, then dried under vacuum and stored under an argon atmosphere in a drybox until further use.

SBA-b. The same grafting procedure was used as described above for **SBA-g1**. 3-Aminopropyltriethoxysilane (0.22 g, 1.0 mmol) was grafted onto SBA-15 (1.0 g) in refluxing toluene (50 mL).

Ring-Opening with Ammonia. Sultone-functionalized silica (0.36 g) was dried under high vacuum at 80°C overnight. After cooling to room-temperature, ammonia was added to the evacuated reaction flask via a balloon. After 24 hours, the ammonia was vented and the solids were acidified by slurrying in 0.5N HCl for 2 hours, followed by filtration, washing with 0.5N HCl (30 mL x 3) and water (30 mL x 5), and drying under vacuum.

Ring-Opening by Hydrolysis. Sultone-functionalized silica (0.5 g) was added to water (40 mL) and the resulting suspension was stirred at 40°C for 2 days. Then the solids were filtered, washed with water (3 x 30 mL), 0.5 N HCl (3 x 30 mL), and water (4 x 30 mL), and dried under high vacuum overnight. Acid loading was measured by ion-exchanged with 2N NaCl followed by titration of the resulting HCl with 0.01N NaOH.

Catalytic Reaction—Aldol Condensation of Acetone and *p*-Nitrobenzaldehyde. An amount of heterogeneous catalyst corresponding to 25 μmol amine and/or 25 μmol acid (0.1–0.2 g) was added to a vial and dried under high vacuum at 80°C overnight. A solution of *p*-nitrobenzaldehyde (38 mg, 0.25 mmol) in acetone (5 mL) was added and the vial was stirred under an argon atmosphere at 50°C. The reaction products (alcohol and olefin) were quantified by HPLC after filtering to remove the catalyst.

Acknowledgements

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Additional Figures—Thermogravimetry data

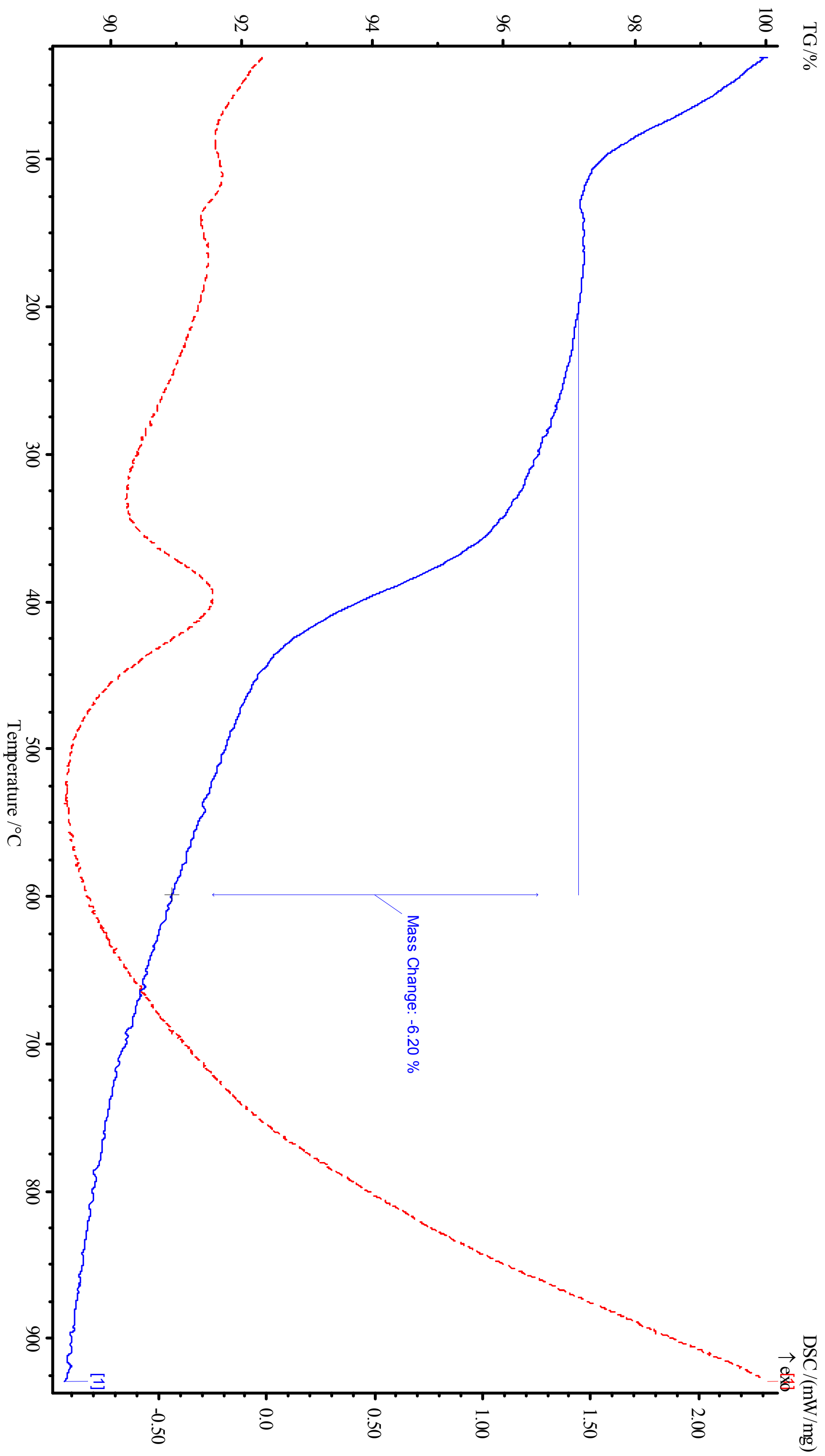

Figure 4.5. TGA trace for **SBA-g1**

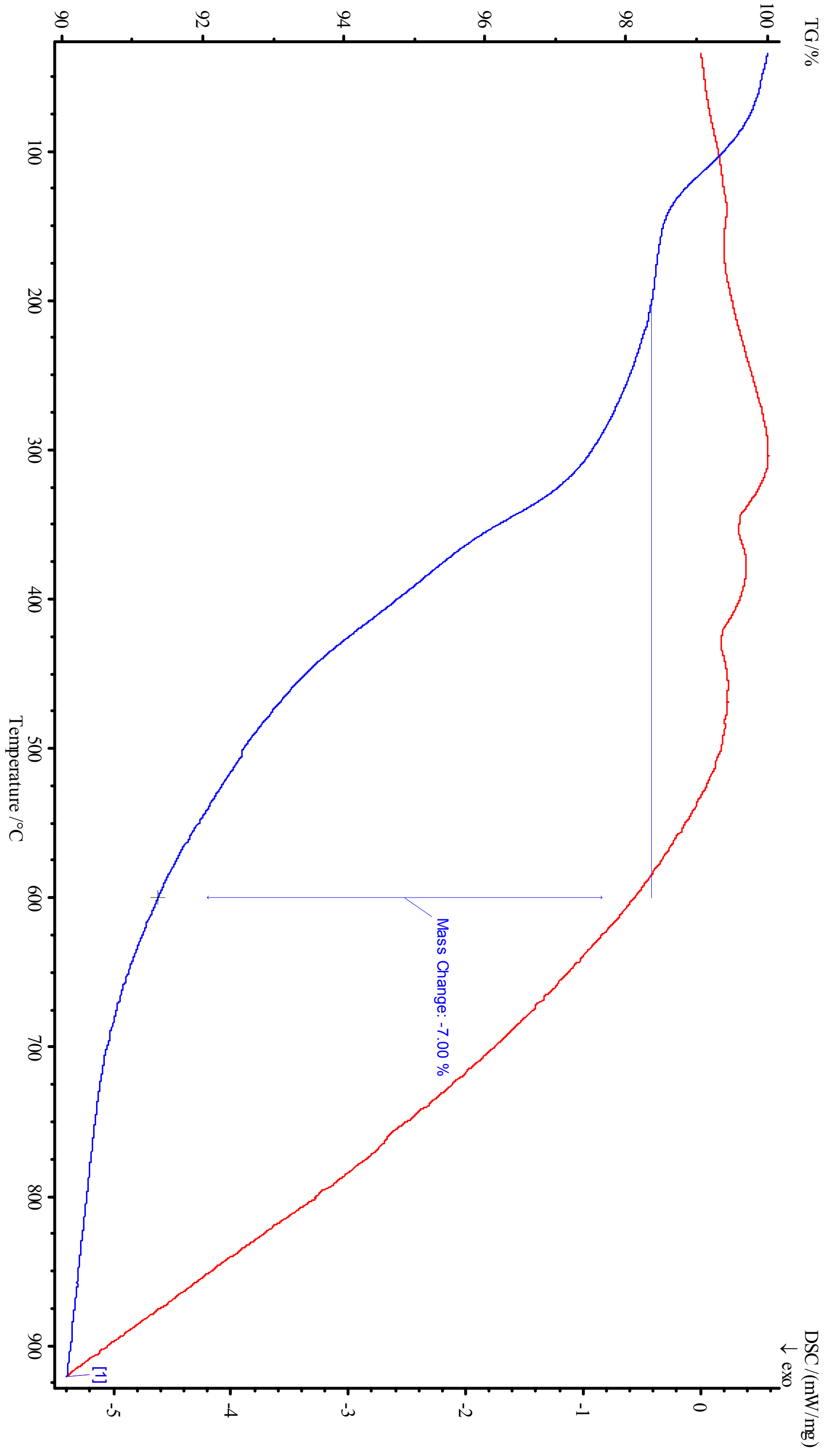

Figure 4.6. TGA trace for **SBA-ab-p**

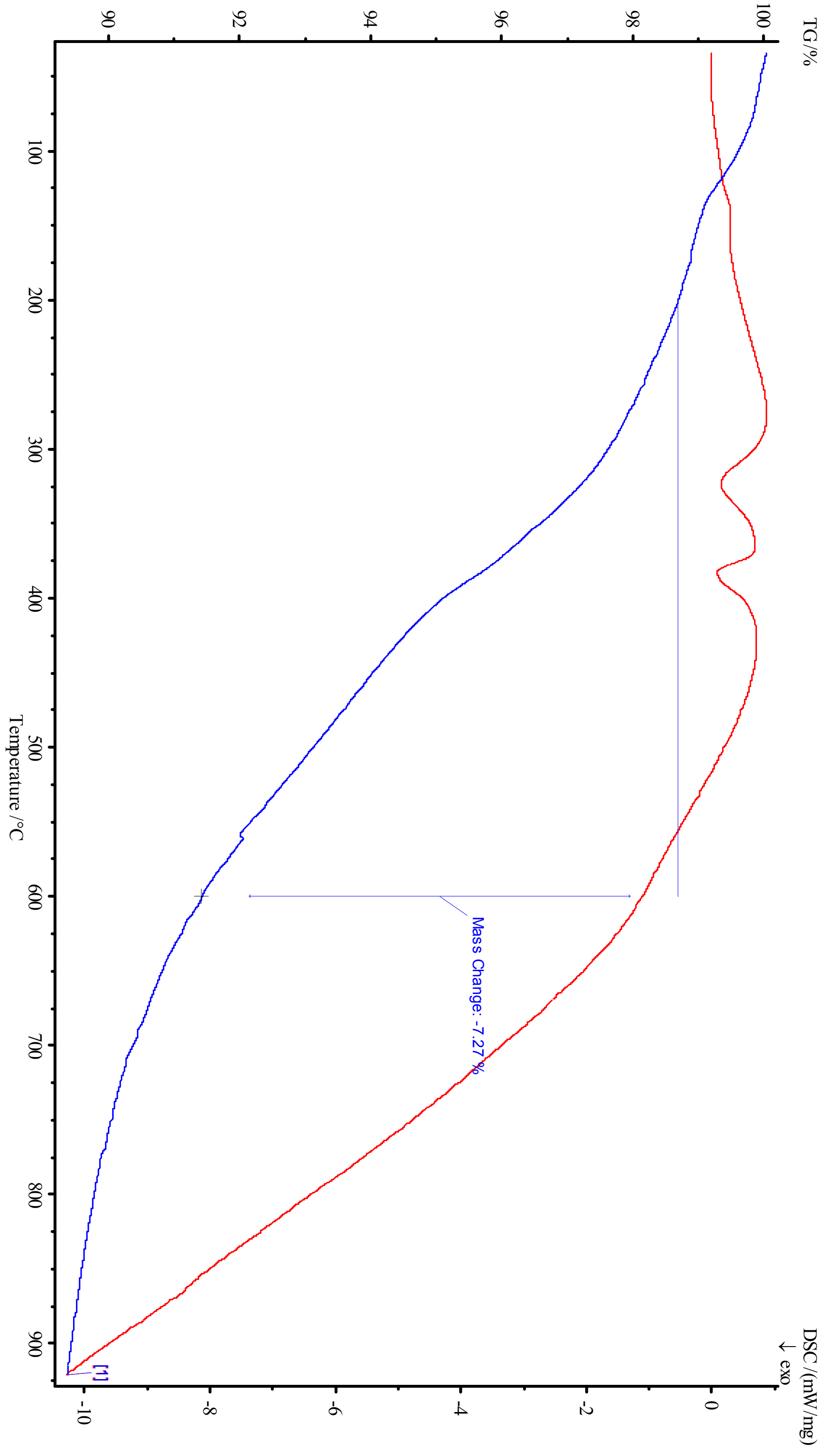

Figure 4.7. TGA trace for **SBA-b**