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# Sulfonic acid functionalized silica: A remarkably efficient heterogeneous reusable catalyst for α-monobromination of carbonyl compounds using *N*-bromosuccinimide☆

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**Abstract**

Sulfonic acid functionalized silica has been found to be a highly efficient and versatile catalyst for α-monobromination of carbonyl compounds (cyclic and acyclic ketones, 1,3-diketones, β-ketoesters, lactones, coumaranones and lactams) using *N*-bromosuccinimide under mild reaction conditions. The α-monobrominated products were obtained in very high yields and in short reaction times. The catalyst works under heterogeneous conditions and can be recyclable.


*Keywords:* Sulfonic acid functionalized silica; Carbonyl compound; α-Monobromination; NBS; Heterogeneous recyclable catalyst

## 1. Introduction

The catalyst which would be useful to make the organic transformations eco-friendly and economically viable are now highly demanded in academic laboratories and industries. Several heterogeneous catalysts are thus finding increasing applications in the field of catalysis [1]. Solid acid-based catalysts have offered simpler, more reactive and more benign alternatives than their homogeneous counterparts [2]. The expensive organic polymer chain in traditional polymer supported catalysts has now been replaced by a silica chain having a covalently anchored organic spacer to create organic–inorganic hybrid (interphase) catalysts [3]. In these heterogeneous catalysts the reactive centers are highly mobile similar to that of homogeneous catalysts and at the same time they can be recovered. Based on this idea various types of sulfonic acid functionalized silica have been considered in catalyzing chemical transformations as Bronsted acid sites can selectively be created here [3,4]. However, to our knowledge, such catalysts have not been used earlier for selective bromination of carbonyl compounds. The catalytic activity of these materials has also not been studied well [3]. Here we report a highly efficient α-monobromination of carbonyl compounds using NBS in the presence of sulfonic acid functionalized silica (Fig. 1) as a catalyst.

α-Bromination of carbonyl compounds is an important organic transformation as the α-brominated products are useful intermediates in organic synthesis [5]. The monobromination of these compounds at the α-position (if the position contains no substituent) is difficult as the disubstituted products are also formed. Bromine in the presence of protic and Lewis acids is generally used for α-bromination of carbonyl compounds [6].

*N*-Bromosuccinamide (NBS) which is a superior brominating agent in term of ease of handling is now being used increasingly for this purpose. NBS is applied for α-bromination of carbonyl compounds in the presence of a radical initiator [such as azabisisobutyronitrile (AIBN) or dibenzyl peroxide (BPO)] [7] or in strongly basic media [8–11] or in the presence of $Mg(ClO_4)_2$ [12], $NH_4OAc$ [13], Amberalyst-15 [14] or $NaHSO_4$ adsorbed on silica gel [15]. However, the preparation of α-monobrominated compounds as the major products is still a problem. Recently to explore the catalytic activity of sulfonic acid functionalized silica we have observed that it is a highly efficient catalyst for α-monobromination of carbonyl compounds using NBS (Scheme 1).

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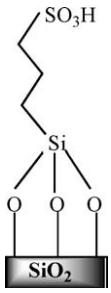
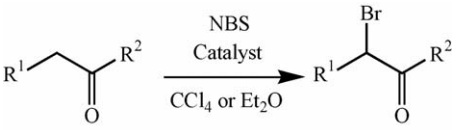



Fig. 1. Sulfonic acid functionalized silica.



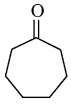
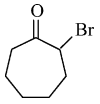
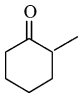
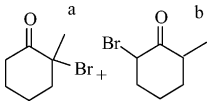
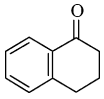
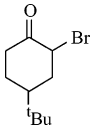
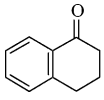
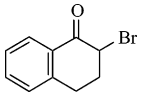
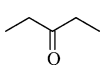
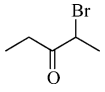
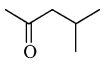
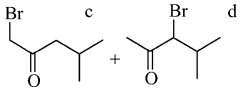
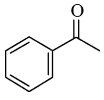
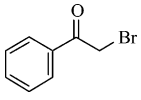

Scheme 1.

## 2. Results and discussion

A wide range of carbonyl compounds were transformed into the corresponding α-monobrominated products by treatment with NBS in the presence of sulfonic acid functionalized silica as a catalyst (Tables 1–3). Both cyclic and acyclic ketones underwent the conversion smoothly at room temperature. The α-monobrominated products were obtained in high yields. With α-substituted cyclic ketones (Table 1, entry d) monobromination took place at both the α-positions but mainly at the substituted position. The times required for conversions of cyclic and acyclic monocarbonyl compounds using sulfonic acid functionalized silica were generally lower compared to the times required with $NaHSO_4{\cdot}SiO_2$ used [15] earlier by us. The present catalyst showed highest activity in $CCl_4$ for α-bromination of cyclic ketones and $Et_2O$ was the next choice as a solvent (Table 4). The conversion was attempted with different other solvents such as $CHCl_3$, $CH_2Cl_2$, THF, $CH_3CN$ and $CH_3OH$. The yields of the products were lower when the reaction was conducted in any of these solvents and the reaction times were also longer. However, with acyclic ketones $CCl_4$ was better than $Et_2O$ as a reaction solvent. An unsymmetrical acyclic ketone (Table 1, entry h) was found to form two products resulted from monobromination at the two α-positions. Previously, the applicability of some α-bromination methods was not reported for acyclic ketones [14].

The present catalyst is highly suitable for α-monobromination of β-dicarbonyl compounds (β-ketoesters and 1,3-dicarbonyl compounds) with NBS at room temperature to afford the products in excellent yields. The preparation of α-monobromo compounds from α-unsubstituted β-ketoester is quite difficult as these bromo compounds are prone to undergo disproportionation to dibrominated and debrominated products. In the present case, the reaction of an α-unsubstituted β-ketoesters with NBS using catalytic amount of sulfonic acid functionalized silica at room temperature afforded the corresponding α-monobromo product in an yield of 95–99% and in short reaction time (0.5–1.0 h) (Table 2, entries a–d).

Table 1
α-Bromination of cyclic and acyclic ketones with NBS catalyzed by sulfonic acid functionalized silica

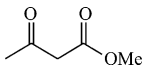
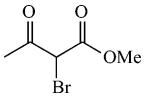
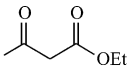
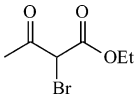
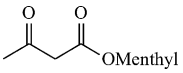
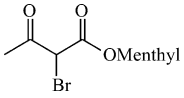
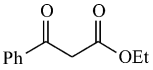
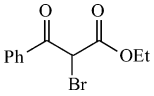
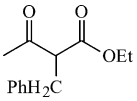
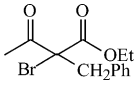
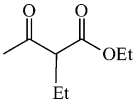
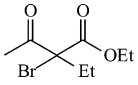
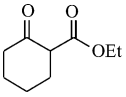
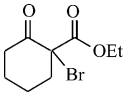
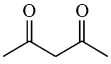
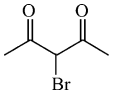
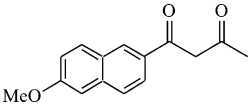
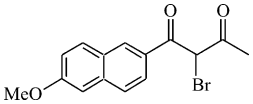
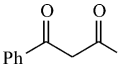
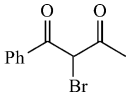
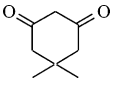
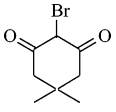
| Entry | Substrate | Product (**1**) | Time (h) | Isolated yield (%) |
|---|---|---|---|---|
| a |  |  | 0.5 | 95 |
| b |  |  | 0.5 | 91 |
| c |  |  | 0.5 | 93 |
| d |  |  | 1.0 | 94 and 3, respectively |
| e |  |  | 0.5 | 95 |
| f |  |  | 1.0 | 99 |
| g |  |  | 0.5 | 87 |
| h |  |  | 1.0 | 72 and 10, respectively |
| i |  |  | 2.0 | 72 |

a, b, c and d are products referred as **1d$_1$**, **1d$_2$**, **1h$_1$** and **1h$_2$**.

No trace of dibrominated product could be found in the reaction. α-Monosubstituted β-ketoesters also produced the α-brominated products in almost similar yields. $Et_2O$ was found to be the suitable solvent for the conversion of β-dicarbonyl compounds. Our earlier method using $NaHSO_4{\cdot}SiO_2$ [15] was not so efficient for α-monobromination of α-unsubstituted 1,3-dicarbonyl compounds as the yields (∼70%) were not very high. This method [15] and several other earlier reported methods [12,13,16] were associated with the formation of dibromo compounds. However, the quantitative yields of the monobrominated 1,3-dicarbonyl compounds in the present method make it of a great synthetic utility.

Sulfonic acid functionalized silica was also successfully applied for α-bromination of lactams, lactones and coumaranones. For lactams the conversion was carried out at 80 °C in $CCl_4$ while for lactones and coumaranones the conversion underwent smoothly at room temperature in the same solvent.

Table 2
α-Bromination of 1,3-dicarbonyl compounds with NBS catalyzed by sulfonic acid functionalized silica

| Entry | Substrate | Product (**2**) | Time (h) | Isolated yield (%) |
|---|---|---|---|---|
| a |  |  | 1.0 | 95 |
| b |  |  | 0.75 | 98 |
| c |  |  | 0.5 | 98 |
| d |  |  | 0.75 | 99 |
| e |  |  | 1.5 | 98 |
| f |  |  | 1.5 | 95 |
| g |  |  | 1.5 | 97 |
| h |  |  | 1.0 | 91 |
| i |  |  | 0.75 | 98 |
| j |  |  | 0.75 | 95 |
| k |  |  | 0.75 | 96 |

Previous studies on such conversions using NBS are limited [2]. A combination of $Mg(ClO_4)_2$ and NBS was reported earlier for α-bromination of amides [12]. The present protocol produces the α-monobrominated lactams, lactones and coumaranones in high yields. The structures of all the products were established from their spectroscopic (IR, $^1$H NMR and MS) data.

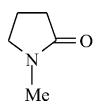
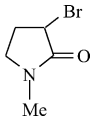
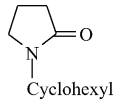
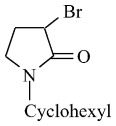
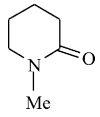
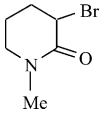
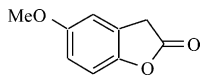
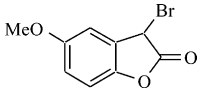
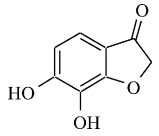
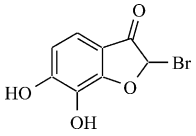
The catalyst, sulfonic acid functionalized silica, was prepared following the known procedure [3] by immobilization of propyl thiol group on silica using 3-mercaptopropyl trimethoxy silane followed by selective oxidation of the thiol groups by aqueous $H_2O_2$ to sulfonic acid groups. Silica gel is less expensive and readily available but it possesses the capacity of anchoring of organic chain easily. The experimental procedure of the present conversion is simple. The catalyst works under heterogeneous conditions and can easily be handled and removed from the reaction mixture. It can be recovered and recycled. It was utilized consecutively three times without loss of its activity.

## 3. Experimental section

### 3.1. General procedure

Sulfonic acid functionalized silica (60 mg) was added to a mixture of carbonyl compound (1 mmol) and NBS (1.2 mmol)

Table 3
α-Bromination of lactams and coumaranones with NBS catalyzed by sulfonic acid functionalized silica

| Entry | Substrate | Product (**3**) | Time (h) | Isolated yield (%) |
|---|---|---|---|---|
| a |  |  | 2.0 | 96 |
| b |  |  | 3.0 | 87 |
| c |  |  | 3.0 | 71 |
| d |  |  | 0.25 | 98 |
| e |  |  | 2.0 | 73 |

in $CCl_4$ or $Et_2O$ (5 ml). The mixture was stirred at room temperature or heated at 80 °C (for only lactam). The reaction was monitored by TLC. After completion the mixture was filtered. The catalyst was washed with $CHCl_3$ (2 × 10 ml), EtOH (2 × 10 ml) and ether (2 × 10 ml) for recyclization purpose. The filtrate was concentrated and the residue was subjected to column chromatography over silica gel using hexane–EtOAc (10:1) as eluent to obtain pure α-monobrominated product.

Spectroscopic (IR, $^1$H NMR and MS) data of unknown and some representative α-monobromo compounds are given below.

*3.1.1. 2-Bromo-1-tetralone (**1f**)*

IR (neat): 1685, 1583, 1462, 1374 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 8.22 (1H, dd, $J$ = 8.0, 2.0 Hz), 7.62–7.54 (3H, m), 4.06 (1H, t, $J$ = 6.0 Hz), 2.36–2.34 (1H, m), 2.31–2.29 (1H, m), 2.28–2.24 (2H, m); EIMS: (*m*/*z*) 226, 224 ($M^{+\bullet}$); Anal. Calcd. for $C_{10}H_9BrO$: C, 53.33; H, 4.00. Found: C, 53.42; H, 4.04.

Table 4
Solvent effect in the reaction of cyclohexanone (**A**) and ethyl acetoacetate (**B**) with NBS catalyzed by sulfonic acid functionalized silica

| Entry | Solvent | Time (h) for | | Isolated yield (%) from | |
|---|---|---|---|---|---|
| | | **A** | **B** | **A** | **B** |
| a | $CCl_4$ | 0.5 | 1.0 | 95 | 94 |
| b | $CHCl_3$ | 10 | 3.0 | 70 | 87 |
| c | $CH_2Cl_2$ | 10 | 5.0 | 47 | 84 |
| d | $Et_2O$ | 0.5 | 0.75 | 90 | 98 |
| e | THF | 10 | 7.0 | 42 | 69 |
| f | $CH_3CN$ | 10 | 5.0 | 71 | 88 |
| g | $CH_3OH$ | 10 | 5.0 | 53 | 72 |

*3.1.2. 1-Bromo-4-methyl-pentane-2-one (**1h$_1$**)*

IR (neat): 1710, 1462, 1376, 1183 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 3.76 (2H, s), 2.54 (2H, d, $J$ = 7.0 Hz), 1.79 (1H, m), 0.94 (6H, d, $J$ = 7.0 Hz); EIMS: *m*/*z* 180, 178 ($M^{+\bullet}$); Anal. Calcd. for $C_6H_{11}BrO$: C, 40.22; H, 6.15. Found: C, 40.17; H 6.18.

*3.1.3. 3-Bromo-4-methyl-pentane-2-one (**1h$_2$**)*

IR (neat): 1712, 1460, 1385, 1205 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 3.97 (1H, d, $J$ = 7.0 Hz), 2.37 (3H, s), 1.61 (1H, m), 0.91 (6H, d, $J$ = 7.0 Hz); EIMS: *m*/*z* 180, 178 ($M^{+\bullet}$); Anal. Calcd. for $C_6H_{11}BrO$: C, 40.22; H, 6.15. Found: C, 40.26; H, 6.12.

*3.1.4. 2-Bromo-3-oxo-ethylbutanoate (**2b**)*

IR (neat): 1718, 1462, 1227 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 4.67 (1H, s), 4.28 (2H, q, $J$ = 7.0 Hz), 2.43 (3H, s), 1.32 (3H, t, $J$ = 7.0 Hz); EIMS: *m*/*z* 210, 208 ($M^{+\bullet}$); Anal. Calcd. for $C_6H_9BrO_3$: C, 34.45; H, 4.31. Found: C, 34.50; H, 4.27.

*3.1.5. 2-Bromo-3-oxo-3-phenyl, ethylpropanoate (**2d**)*

IR (neat): 1759, 1738, 1687, 1596, 1449 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 7.99 (2H, dd, $J$ = 8.0, 2.0 Hz), 7.63–7.42 (3H, m), 4.25 (2H, q, $J$ = 7.0 Hz), 1.23 (3H, t, $J$ = 7.0 Hz); EIMS: *m*/*z* 272, 270 ($M^{+\bullet}$); Anal. Calcd. for $C_{11}H_{11}BrO_3$: C, 48.71; H, 4.06. Found: C, 48.63; H, 4.11.

*3.1.6. 2-Bromo-1-(6-methoxy-2-napthyl)-3-oxo-butane-1-one (**2i**)*

IR (neat): 1624, 1592, 1480, 1458 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$): δ 8.40 (1H, d, $J$ = 2.0 Hz), 7.96 (1H, d, $J$ = 8.0 Hz), 7.82 (1H, d, $J$ = 8.0 Hz), 7.71 (1H, dd, $J$ = 8.0, 2.0 Hz), 7.18 (1H, dd, $J$ = 8.0, 2.0 Hz), 7.09 (1H, d, $J$ = 2.0 Hz), 5.67 (1H, s), 3.93 (3H,

s), 2.44 (3H, s); EIMS: *m/z* 322, 320 ($M^{+\bullet}$); Anal. Calcd. for $C_{15}H_{13}BrO_3$: C, 56.07; H, 4.05. Found: C, 56.21; H, 4.01.

*3.1.7. 2-Bromo-5,5′-dimethyl-cycloxane-1,3-dione (**2k**)*

IR (neat): 1625, 1577, 1450, 1323 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 6.40 (1H, s), 2.52 (2H, s), 2.43 (2H, s), 1.12 (6H, s); EIMS: *m/z* 220, 218 ($M^{+\bullet}$); Anal. Calcd. for $C_8H_{11}BrO_2$: C, 43.83; H, 5.02. Found: C, 43.85; H 4.96.

*3.1.8. 3-Bromo-1-cyclohexyl, pyrrolidine-2-one (**3b**)*

IR (neat): 1702, 1451, 1375, 1346 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 4.57 (1H, dd, $J = 12.0$, 5.0 Hz), 2.90–2.82 (4H, m), 2.64–2.55 (11H, m); EIMS: *m/z* 247, 245 ($M^{+\bullet}$); Anal. Calcd. for $C_{10}H_{16}BrNO$: C, 48.78; H, 6.50. Found: C, 48.73; H, 6.39.

*3.1.9. 3-Bromo-5-methoxy, coumarane-2-one (**3d**)*

IR (neat): 1798, 1606, 1485, 1358 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.08–6.72 (3H, m), 5.40 (1H, s), 3.67 (3H, s); EIMS: *m/z* 244, 242 ($M^{+\bullet}$); Anal. Calcd. for $C_9H_7BrO_3$: C, 44.44; H, 2.88. Found: C, 44.32; H, 2.87.

*3.1.10. 2-Bromo-6,7-dihydroxy, coumarane-3-one (**3e**)*

IR (neat): 3422, 1649, 1482, 1443 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 7.68 (1H, brs), 7.22 (1H, brs), 6.92 (1H, d, $J = 8.0$ Hz), 6.48 (1H, d, $J = 8.0$ Hz), 5.38 (1H, s); EIMS: *m/z* 246, 244 ($M^{+\bullet}$); Anal. Calcd. for $C_8H_5BrO_4$: C, 39.18; H, 2.04. Found: C, 39.26; H, 2.09.

## 4. Conclusions

In conclusion we have demonstrated that sulfonic acid functionalized silica is a remarkably efficient catalyst for α-monobromination of a wide range of carbonyl compounds using NBS. The present protocol is associated with several advantages such as mild reaction conditions, short reaction times, excellent yields of monobrominated products, simple experimental procedure and reusability of the catalyst. The used catalyst makes the process more eco-friendly compared to the homogeneous acid catalysts. A novel important application of the present catalyst is also discovered.

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## References

[1] (a) A. Corma, Chem. Rev. 95 (1995) 559;
(b) A. Corma, H. Garcia, Catal. Today 38 (1997) 257.
[2] B. Karimi, D. Zareyee, Tetrahedron Lett. 46 (2005) 4661.
[3] (a) A. Shylesh, S. Sharma, S.P. Mirjkar, A.P. Singh, J. Mol. Catal. A: Chem. 212 (2004) 219;
(b) B. Karimi, M.J. Khalkhali, Mol. Catal. A: Chem. 232 (2005) 113.
[4] (a) I. Diaz, C. Marquez-Alvarez, F. Mohino, J. Perez-Pariente, E. Sastre, J. Catal. 193 (2000) 295;
(b) I.K. Mbaraka, D.R. Radu, V.S. Lin, B.H. Shanks, J. Catal. 219 (2003) 329.
[5] R.C. Larock, Comprehensive Organic Transformations, 2nd ed., VCH Publishers Inc., New York, 1999, pp. 715–719.
[6] (a) L.A. Bigelow, R.S. Hanslick, Organic Synthesis Collection, vol. 2, Wiley, New York, 1943, p. 244;
(b) E.W. Garbisch Jr., J. Org. Chem. 30 (1965) 2109;
(c) P. Dowd, C. Kaufman, P. Kaufman, J. Org. Chem. 50 (1985) 882;
(d) K. Hakam, M. Thielmann, T. Thielmann, E. Winterfeldt, Tetrahedron 43 (1987) 2035.
[7] H. Schmid, P. Karrer, Helv. Chem. Acta 29 (1946) 573.
[8] D.P. Curran, E. Bosch, J. Kaplan, M. Newcomb, J. Org. Chem. 54 (1985) 1826.
[9] D.P. Curran, C.T. Chang, J. Org. Chem. 54 (1989) 3140.
[10] S. Karimi, K.G. Grohmann, L. Todaro, J. Org. Chem. 60 (1995) 554.
[11] R.E. Boyd, C.R. Rasmussen, J.B. Press, Synth. Commun. 25 (1995) 1045.
[12] D. Yang, Y.-L. Yan, B. Lui, J. Org. Chem. 67 (2002) 7429.
[13] K. Tanemura, T. Suzuki, Y. Nishida, K. Satsumabayashi, T. Horaguchi, Chem. Commun. (2004) 470.
[14] H.M. Meshram, P.N. Reddy, K. Sadashiv, J.S. Yadav, Tetrahedron Lett. 46 (2005) 623.
[15] B. Das, K. Venkateswarlu, G. Mahender, I. Mahender, Terahedron Lett. 46 (2005) 3041.
[16] L.M. Matthew, R.M. Yogesh, M.W. Steven, Tetrahedron Lett. 46 (2005) 4749.