Tetrahedron Letters 52 (2011) 6113–6117

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

The hydroamination of alkenes with sulfonamides catalyzed by the recyclable silica gel supported triflic acid

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ARTICLE INFO

Article history:
Received 16 June 2011
Revised 29 August 2011
Accepted 6 September 2011
Available online 10 September 2011

Keywords:
Hydroamination
Triflic acid
Supported catalyst
Alkene
Sulfonamide

ABSTRACT

The vast applications of triflic acid (TfOH) in catalysis are severely limited by its corrosive and fuming properties. Immobilization of TfOH on silica gel well solves these problems and affords efficient recovery and reusability of TfOH. Two types of supported TfOH, the prepared silica gel supported TfOH and the in situ silica gel adsorbed TfOH, both exhibit good catalytic activity and reusability in the hydroamination of alkene with sulfonamide. The in situ silica gel adsorbed catalyst has been used for 5 runs with maintained reactivities and yields, which are superior to the performance of the prepared silica gel supported TfOH. For a series of alkenes and various sulfonamides, the heterogeneous hydroamination reactions catalyzed by both types of silica gel supported TfOH to afford similar moderate to excellent yields.

Introduction

The synthesis of amines from the simple chemicals, such as alkenes is a very important area in modern organic chemistry, due to the extraordinary importance of the amine compounds in the synthesis of natural products, fine chemicals and drugs.[1] The intermolecular hydroamination of alkenes with sulfonamides has attracted considerable interest in recent years because of the atom-economy feature[2] and the easy transformation of the hydroamination products to amines via N-desulfonylation.[3] Recently, platinum(II),[4] gold(I),[5] copper(II),[6] and other metal salts[7] have been explored as effective catalysts for the hydroamination of alkenes with sulfonamides. Moreover, NBS[8] and a series of Brønsted acids, such as $[PhNH_3][B(C_6F_5)_4]$,[9] triflic acid,[10] *H*-montmorillonite,[11] heteropoly acids[12], and SO_3H-functionalized ionic liquids[13] have also been described to be effective catalysts for the intermolecular hydroamination of alkenes with sulfonamides. Although prominent progress has been achieved in the homogeneous hydroamination of alkenes with sulfonamides, the heterogeneous reactions catalyzed by the reusable supported catalysts still remain to explore.[14]

With the demanding for ‘green chemistry’, the immobilization of the homogeneous catalysts to the solid supporters such as silica gel has attracted great interest,[15] because easy separation of the products and efficient recovery of the catalysts can be achieved through simple filtration. Moreover, the applications of the supported catalysts in the continuous flow-type processes are potentially allowed, which are important in the industry. Triflic acid (TfOH), namely super acid,[16] is perhaps the most versatile Brønsted acid catalyst in a vast stretch of organic reactions,[17] but its applications are severely limited by the corrosive and fuming properties which cause problems in handling, transportation, and disposal. Recently, we have prepared the silica gel supported TfOH which solves the corrosive and fuming problems of TfOH. Although the silica gel supported TfOH has been successfully applied to the addition of β-dicarbonyl compounds to alcohols and alkenes,[18] the preparation procedures of the silica gel supported TfOH are still tedious and inevitably consume the solvent and energy. In a successive endeavor to explore more effective methods to immobilize TfOH and the further applications of the silica gel supported TfOH, we herein report the immobilization of TfOH through two different approaches and their applications in catalyzing the heterogeneous hydroamination of alkenes with sulfonamides.

Results and discussion

The hydroamination of 1a with 2a catalyzed by the prepared TfOH–SiO_2

As the first stage of this study, the silica gel supported TfOH (TfOH–SiO_2) was prepared through adsorption of TfOH onto silica

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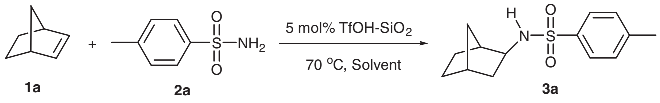
doi:10.1016/j.tetlet.2011.09.025

gel.[18] The prepared TfOH–SiO_2 was then used as the catalyst for the hydroamination of norbornylene (**1a**) with *p*-toluenesulfonamide (**2a**). It can be seen from Table 1 that the prepared TfOH–SiO_2 can not catalyze the reactions of **1a** and **2a** in *n*-heptane, THF, methanol, acetonitrile, and nitromethane at 70 °C (Table 1, entries 1–5). As dioxane, ethyl acetate, and 1,2-dichloroethane (DCE) were used as the solvents, better reaction results were obtained and even 96% yield was observed in chloroform (Table 1, entries 6–9). When toluene was used as the solvent for the hydroamination of **1a** with **2a**, we were delighted to obtained very good 98% yield after 4 h at 70 °C. To expel the possibility that the reaction was catalyzed by the leached TfOH, we stirred TfOH–SiO_2 in toluene at 70 °C for 4 h, then filtered out the solid catalyst at 70 °C, and added **1a** and **2a** to the resulting solution and stirred at 70 °C for 4 h, but no product was detected. The result proves that the hydroamination of **1a** with **2a** is a heterogeneous reaction catalyzed by the supported TfOH rather than the homogeneous reaction catalyzed by the leached TfOH. Moreover, the prepared TfOH–SiO_2 was recovered readily and reused for 3 runs with almost maintained reactivities and yields, but it lost the catalytic ability in the 4th run (Table 1, entries 10–13). To investigate the catalytic reactivities of the fresh and recovered TfOH–SiO_2 in the reactions of **1a** and **2a**, the conversions of the consecutive reactions at different times were monitored by HPLC. The results showed that the recovered TfOH–SiO_2 in the 2nd and 3rd runs possessed the same or even better catalytic reactivities in comparison with the fresh TfOH–SiO_2. Why did the reactivity of the 4th reaction drop sharply? Firstly, we observed that the color of the reaction mixture in the 3rd run turned to deep brown from light yellow, indicating the decomposition of TfOH. Moreover, in the consecutive reactions, through the elemental analysis of F and S in TfOH–SiO_2 after each reaction, we demonstrated that 5–8% of TfOH leaches out from TfOH–SiO_2 in one cycle of reaction.[18] So, we propose that the remarkable decrease of reactivity in the 4th run is deduced by the decomposition and the leaching of TfOH. If the ratio of **1a**–**2a** was changed from 2:1 to 1:1 or 1:2, worse reaction results were observed (Table 1, entries 14, 15). Note that the reaction of **1a** and **2a** did not proceed at room temperature (Table 1, entry 16). Moreover, when silica gel without TfOH was used as the catalyst, the reaction of **1a** and **2a** did not proceed, illustrating that silica gel only acted as the supporter of TfOH and did not catalyze the reaction. At last, the homogeneous reaction of **1a** and **2a** with 5% TfOH as the catalyst was carried out and 93% yield was obtained (Table 1, entry 17). This control experiment reveals that the heterogeneous reaction with silica gel as the adsorbent is a little superior to the homogeneous reaction (98% vs 93% yield).

Table 1
The hydroamination of **1a** with **2a** catalyzed by the prepared TfOH–SiO_2[a]



Entry	Run	Solvent	**1a**:**2a**	Yield[b] (%)
1	1	*n*-Heptane	2:1	0
2	1	THF	2:1	0
3	1	Methanol	2:1	0
4	1	Acetonitrile	2:1	5
5	1	Nitromethane	2:1	5
6	1	Dioxane	2:1	23
7	1	Ethyl acetate	2:1	59
8	1	DCE	2:1	91
9	1	Chloroform	2:1	96
10	1	Toluene	2:1	98
11	2	Toluene	2:1	97
12	3	Toluene	2:1	93
13	4	Toluene	2:1	4
14	1	Toluene	1:1	58
15	1	Toluene	1:2	49
16[c]	1	Toluene	2:1	0
17[d]	1	Toluene	2:1	93

[a] Reagents and conditions: **1a** (2.0 mmol), **2a** (1.0 mmol), TfOH–SiO_2 (0.10 g, containing 0.05 mmol TfOH), solvent (2 mL), 70 °C, 4 h unless noted.

[b] Isolated yields based on the sulfonamide.

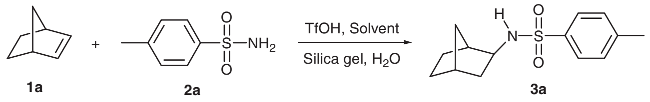
[c] This reaction was carried out at 25 °C for 28 h.

[d] The reaction was carried out with liquid TfOH (5 mol %) as the catalyst.

The hydroamination of 1a with 2a catalyzed by the in situ silica gel adsorbed TfOH

Although the immobilization of TfOH on the silica gel well solves the problems caused by the corrosive and fuming properties of TfOH, the preparation procedures for the silica gel supported triflic acid still consume much solvent and energy. If the recovery and reusability of TfOH could be achieved by directly adding silica gel as the adsorbent of TfOH, the procedures to prepare the silica gel supported TfOH would be avoided and TfOH could be recovered and reused much more conveniently. So, we attempted to adsorb TfOH onto the silica gel by directly adding the silica gel to the toluene solution containing TfOH. When silica gel (200–300 mesh, 0.1 g) was added to the toluene solution (2 mL) containing TfOH (4.4 μL, 0.05 mmol), the foggy solution became clear immediately, indicating that TfOH was adsorbed by the silica gel. The resulting mixture was stirred for 30 min at room temperature and **1a** (2 mmol) and **2a** (1 mmol) were added. The hydroamination of **1a** with **2a** at 70 °C gave excellent 95% yield after 4 h and the catalyst was readily recovered by simple filtration. In the subsequent reaction of **1a** with **2a**, we were delighted to find that the in situ silica gel adsorbed TfOH can be used for 4 runs with maintained reactivity and yields (entries 1, 2, Table 2). It is well known that silica gel contains lots of hydroxyl groups which can bind water firmly via hydrogen bonds. On the other hand, TfOH is miscible with water. So, with the hope to reduce the leaching of TfOH from silica gel in the hydrophobic solvent, thus to improve the reusability of the silica gel adsorbed TfOH, we added a small amount of water to the in situ silica gel adsorbed TfOH. It can be seen from Table 2 that this strategy does work and the best reusability of 5

Table 2
The hydroamination of **1a** with **2a** catalyzed by the in situ silica gel adsorbed TfOH[a]



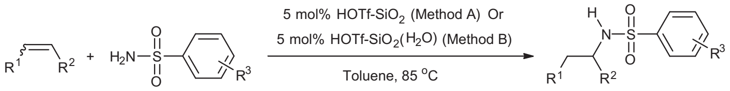
Entry	TfOH (mol %)	H_2O: silica gel	Solvent	Run	Yield[b] (%)
1	5	0	Toluene	1–4	93–95
2	5	0	Toluene	5	8
3	5	1:10	Toluene	1–4	92–95
4	5	1:10	Toluene	5	17
5	5	1:5	Toluene	1–5	92–97
6	5	1:5	Toluene	6	24
7	5	3:10	Toluene	1–4	92–96
8	5	3:10	Toluene	5	12
9	5	1:5	DCE	1–3	92–95
10	5	1:5	DCE	4	0
11	3	1:5	Toluene	1–3	93–94
12	3	1:5	Toluene	4	9
13[c]	5	-	Toluene	1	91

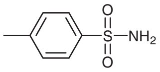
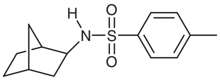
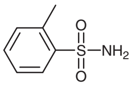
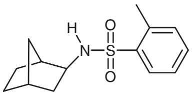
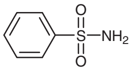
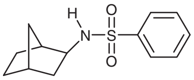
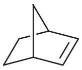
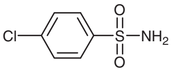
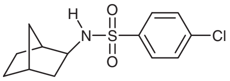
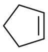
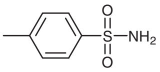
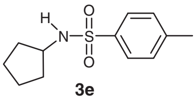
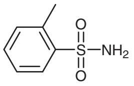
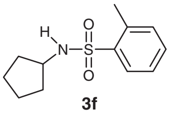
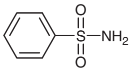
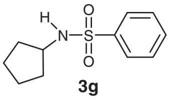
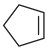
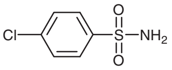
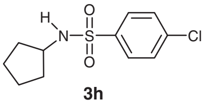
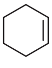
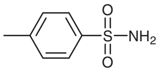
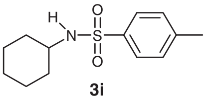
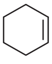
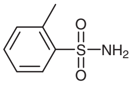
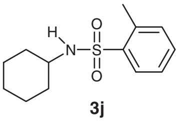
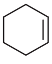
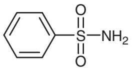
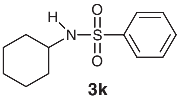
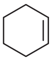
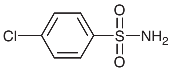
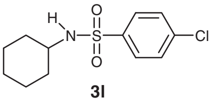
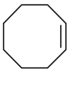
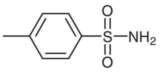
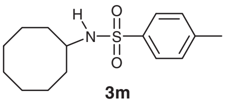
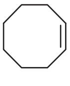
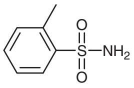
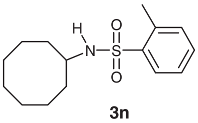
[a] Reagents and conditions: **1a** (2.0 mmol), **2a** (1.0 mmol), TfOH (4.4 μL, 0.05 mmol), silica gel (0.1 g), solvent (2 mL), 70 °C, 4 h unless noted.

[b] Isolated yields based on **2a**.

[c] The reaction was carried out with liquid TfOH (4.4 μL, 0.05 mmol) and H_2O (0.02 mL) as the catalyst.

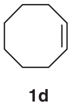
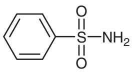
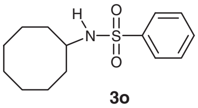
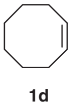
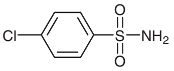
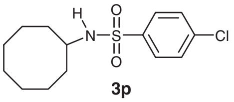
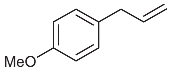
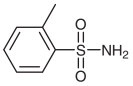
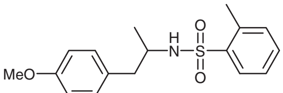
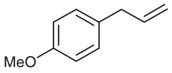
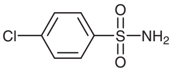
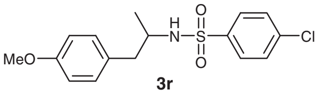
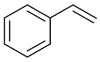
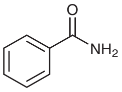
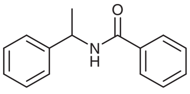
Table 3
The hydroamination of alkenes with sulfonamides catalyzed by both types of silica gel supported TfOH



Entry	Alkene	Sulfonamide	Product	Yield[a] (Method A)[b]	Yield[a] (Method B)[c]
1[d]	 **1a**	 **2a**	 **3a**	95	95
2	 **1a**	 **2b**	 **3b**	72	93
3	 **1a**	 **2c**	 **3c**	95	95
4	 **1a**	 **2d**	 **3d**	88	94
5	 **1b**	 **2a**	 **3e**	74	84
6	 **1b**	 **2b**	 **3f**	88	43
7	 **1b**	 **2c**	 **3g**	71	65
8	 **1b**	 **2d**	 **3h**	86	30
9	 **1c**	 **2a**	 **3i**	93	87
10	 **1c**	 **2b**	 **3j**	88	82
11	 **1c**	 **2c**	 **3k**	74	70
12	 **1c**	 **2d**	 **3l**	91	86
13	 **1d**	 **2a**	 **3m**	67	73
14	 **1d**	 **2b**	 **3n**	65	64

(*continued on next page*)

Table 3 (*continued*)

Entry	Alkene	Sulfonamide	Product	Yield[a] (Method A)[b]	Yield[a] (Method B)[c]
15	 **1d**	 **2c**	 **3o**	72	68
16	 **1d**	 **2d**	 **3p**	57	70
17	 **1e**	 **2b**	 **3q**	91	94
18	 **1e**	 **2d**	 **3r**	72	85
19[f]	 **1f**	 **2e**	 **3s**	89	N. P.[e]

[a] Isolated yield based on the sulfonamide.

[b] Reagents and conditions of method A: alkene (4 mmol), sulfonamide (1 mmol), prepared TfOH–SiO_2 (0.100 g, containing 0.05 mmol TfOH), toluene (2 mL), 85 °C, 20 h unless noted.

[c] Reaction conditions of method B: alkene (4 mmol), sulfonamide (1 mmol), TfOH (4.4 μL, 0.05 mmol), silica gel (0.1 g), H_2O (20 μL), toluene (2 mL), 85 °C, 20 h unless noted.

[d] Alkene: 2 mmol, reaction time: 4 h, temperature: 70 °C.

[e] N. P. means no product.

[f] TfOH–SiO_2 (0.200 g, containing 0.10 mmol TfOH) was used.

runs with maintained reactivity and yields is achieved when appropriate amount of water (20 μL, silica gel:H_2O = 5:1) is added to the first batch of reaction mixture (entries 3–8, Table 2). Through testing the catalytic ability of the hot solution filtered the solid catalyst, we also confirmed that the hydroamination of **1a** with **2a** did be a heterogeneous reaction catalyzed by the supported TfOH rather than the homogeneous reaction catalyzed by the leached TfOH. The conversions in every consecutive reactions were also monitored by HPLC and similar catalytic reactivities were observed in different batches of the in situ silica gel adsorbed TfOH, which were comparable with the prepared TfOH–SiO_2 catalyst. Moreover, the color change of the reaction mixture from light yellow to deep brown was also observed in the 5th reaction, so we similarly attribute the reactivity drop in the 6th reaction mixture to the decomposition and the leaching of TfOH. When 1,2-dichloroethane (DCE) was used as the solvent, the hydroamination of **1a** with **2a** afforded similar yield and reactivity, but the reusability of the catalyst decreased to 3 runs (entries 9 and 10, Table 2). When the catalyst loading was decreased to 3 mol %, the hydroamination also proceeded smoothly but the reusability of the catalyst decreased as well (entries 11 and 12, Table 2). It is noteworthy that without adding the silica gel as the adsorbent, the reaction of **1a** and **2a** with 5 mol % liquid TfOH as the catalyst only gave 91% yield in the presence of H_2O (entry 13, Table 2), indicating that the addition of silica gel is beneficial for the catalytic reaction.

The hydroamination of various alkenes with a series of sulfonamides catalyzed by both types of TfOH–SiO_2

Subsequently, the hydroamination reactions of a series of alkenes with various sulfonamides were examined using the prepared TfOH–SiO_2 (Method A) or the in situ adsorbed TfOH–SiO_2(H_2O) (Method B) as the catalysts (Table 3). For most substrates, the reactions under 70 °C could not afford high yields, thus in most cases the reactions were carried out at 85 °C for 20 h with 4:1 molar ratio (alkene/sulfonamide) to achieve high yields. With the prepared TfOH–SiO_2 or the in situ adsorbed TfOH–SiO_2(H_2O) as the catalysts, the reactions of norbornene **1a** with sulfonamides **2a**, **2c,** and **2d** all afforded the exo-products with excellent 88–95% yields. But in the hydroamination of **1a** with ortho-methyl substituted toluenesulfonamide **2b**, in situ adsorbed TfOH–SiO_2(H_2O) demonstrated better results in comparison with the prepared TfOH–SiO_2 (93% vs 72% yields, entry 2, Table 3). For the hydroamination of cylcopentene **1b** with various sulfonamides **2a**–**d**, the products **3e**–**h** were obtained in good or moderate yields with the prepared TfOH–SiO_2 as the catalyst (Table 3, entries 5–8). When in situ adsorbed TfOH–SiO_2(H_2O) was used as the catalyst, products **3e** and **3g** were obtained but the reactions of **1b** with **2b** and **2d** only gave rather low yields (Table 3, entries 5–8). As cyclohexene **1c** was used to react with sulfonamides **2a**–**d**, better results were observed in good to excellent yields with two types of silica gel supported TfOH as the catalysts (Table 3, entries 9–12). When cyclooctene **1d** with bigger ring was used to react with sulfonamides **2a**–**d**, the reactions exhibited similar lower yields with both catalysts, probably because of the less stability of the cyclooctyl cation[19] (Table 3, entries 13–16). The methoxyl substitution on aromatic rings is typically considered unstable under strong Brønsted acid conditions in nucleophilic addition reactions. The previous homogeneous reactions employing 5% TfOH led to the decomposition of allylanisole at 85 °C.[10a] The heterogeneous reactions of allylanisole **1e** with sulfonamides **2b** and **2d** were carried out and good yields were still obtained with both catalysts, demonstrating the tolerance of functional group in the heterogeneous reactions with the silica gel supported TfOH as the catalysts (Table 3, entries 17 and 18). Note that in these reactions, anti-Markovnikov's rule products were not observed. When allylanisole **1e** reacted with sulfonamides **2a** and **2c**, the reactions also proceeded in moderate yields but the pure products could not be isolated because of the existing inseparable rearrangement products. In an effort to expand the substrate scope, styrene **1f** was used to react with amide **2e** with the prepared TfOH–SiO_2 as the catalyst at enhanced catalyst loading (10 mol %), and the product **3s** was obtained successfully in 89% yield (Table 3, entry 19). Note that with in situ adsorbed TfOH–SiO_2(H_2O) as the catalyst, this reaction did not proceed. The proposed main reason is that the catalytic ability of TfOH in H_2O might be lowered due to the strong binding with H_2O and that was not strong enough to catalyze the reaction of the styrene and amide with comparatively low reactivity.

Conclusions

For the first time, the recovery and recycling of TfOH, a versatile Brønsted acid catalyst, has been realized through directly adding silica gel as the adsorbent to the catalytic reaction mixture. The prepared TfOH–SiO_2 and the in situ adsorbed TfOH–SiO_2(H_2O) have both been successfully applied as the recyclable catalysts for the hydroamination of alkenes with sulfonamides. The in situ adsorbing of TfOH on silica gel not only avoids the procedure to prepare TfOH–SiO_2, but also demonstrates better reusability than the prepared TfOH–SiO_2. For a series of alkenes and various sulfonamides, the hydroamination reactions afforded moderate to excellent yields. Our methods have provided the environmentally friendly protocols possessing the potential for applications in industry. Moreover, the new protocol of in situ adsorbing TfOH on silica gel would open a door to directly achieve the efficient recovery and reusability of various Brønsted acid catalysts and Lewis acid catalysts through simply adding the wet silica gel as the adsorbent to the catalytic reaction mixtures.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (project Nos. 20902020, 21172069), the Innovation Program of Shanghai Municipal Education Commission (Project No. 12ZZ050) and the Fundamental Research Funds for the Central Universities.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.09.025.

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