A Novel Mesoporous Silica-Supported Lewis Acid Catalyst for C–C Bond Formation Reactions in Water

Pentlavalli Sreekanth,[a] Sang-Wook Kim,[b] Taegwhan Hyeon,[b] B. Moon Kim[a,*]

[a] Center for Molecular Catalysis, School of Chemistry and Molecular Engineering, Seoul National University, Seoul, 151–747, South Korea
[b] School of Chemical Engineering, Seoul National University, Seoul, 151–747, South Korea
Tel: (+82)-2-880-6644, Fax: (+82)-2-872-7505, e-mail: kimbm@snu.ac.kr

Received: April 1, 2003; Accepted: June 6, 2003

Abstract: Catalytic allylation of carbonyl compounds in water using tetraallyltin in the presence of lanthanum sulfonate immobilized on mesoporous silica (SBA-15) has been carried out for the first time. The reaction proceeded smoothly in water and furnished the corresponding homoallylic alcohols in good to excellent yields. The catalyst could be reused without significant loss of catalytic activity.

Keywords: allylation; heterogeneous catalysis; lanthanum triflate; Lewis acid; mesoporous silica; water

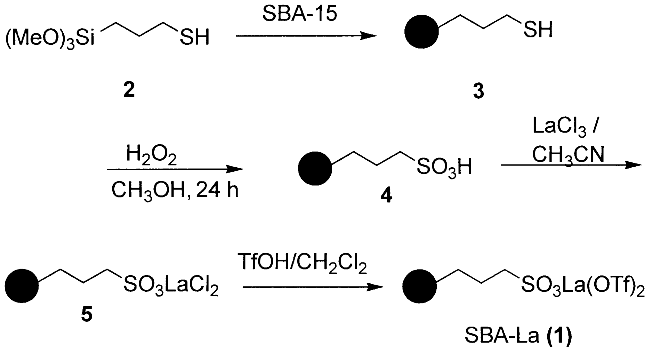
Performing organic reactions in water is one of the fundamental challenges to organic chemists.[1] The use of water as a sole medium of organic reactions would greatly contribute to the development of environmentally friendly processes. Even more desirable is to carry out catalytic organic reactions in water, which normally require delicate reaction conditions in order for the catalyst to be stable and yet reactive. In recent years much attention has been focused on Lewis acid-catalyzed organic reactions in water and several Lewis acid-catalyzed reactions in water have been already identified.[2] Among these are the various catalytic C–C bond formation reactions in water reported by Kobayashi et al.[3–5]

Allylation of carbonyl compounds has become one of several important carbon-carbon bond forming reactions in organic synthesis.[6] The reaction adds a new functionality into a carbonyl substrate, which can then be extended to other functional groups through further organic transformations of the resulting homoallylic alcohol. Such reactions can be achieved by use of metals such as tin, copper/manganese,[7] calcium and germanium.[8] Also, often these reactions can be performed on unprotected carbohydrate substrates in protic media under mild conditions. Nevertheless, it is necessary that most of these reactions be carried out with an acidic co-reagent such as ammonium chloride or hydrobromic acid, and co-solvents such as mixtures of THF and water. To increase the efficiency of the allylation, chemists have been searching for effective catalysts, easy separation techniques and benign solvents under mild reaction conditions.

The advent of mesoporous materials has raised the general expectation that the catalytic efficiency of microporous zeolites can be expanded to a mesoporous dimension.[9] For the introduction of functionality into the mesoporous structure, surface modification techniques have been intensely developed and, in this regard, a renewed interest is surfacing for the development of efficient grafting methods for various mesoporous silica materials. It is clear that the pore walls of mesoporous materials are easily modified with either purely inorganic or with hybrid, semi-organic functional groups.[10,11]

Herein, we report on the development of a new solid Lewis acid catalyst through immobilization of a rare earth metal on mesoporous silica for the first time.

As shown in Scheme 1, the surface of SBA-15 was modified with a tether molecule containing a sulfhydryl group and the resulting thiol moiety of **3** was oxidized to the sulfonic acid **4** with hydrogen peroxide. Lanthanum metal was introduced by treating **4** with lanthanum chloride and the chloride moiety of the resulting lanthanum sulfonate **5** was exchanged with the trifluoromethanesulfonate (triflate) counterion upon treatment with trifluoromethanesulfonic acid. The catalyst **1** was characterized by elemental, ICP-MS and TEM analyses.

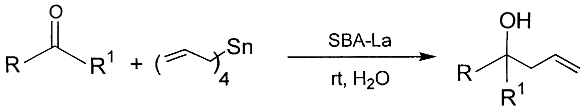


Scheme 1.

DOI: 10.1002/adsc.200303061

From elemental analysis, it was found that the lanthanum sulfonate immobilized on mesoporous silica (SBA-La) contained 4.8% of S, which corresponds to 1.5 mmol/g. ICP-MS verified the existence of the lanthanum metal in catalyst **1**, indicating 0.5 mmol/g of La present in the catalyst. From the above results, the presence of lanthanum triflate [$La(OTf)_2$] in the catalyst was confirmed. TEM images of the catalyst showed that the mesoporous structure of the catalyst remains the same after synthesis of the catalyst and also after recycling experiments.

The catalytic activity of **1** was first tested in the allylation reactions of carbonyl compounds with tetraallytin, which are among the most fundamental and important C−C bond forming reactions. As shown in Scheme 2, various aldehydes and a ketone were chosen as substrates for the allylation reaction in the presence of 1.6 mol % of the catalyst, and a highly efficient allylation reaction has been observed. The results are summarized in Table 1. Aromatic (entries 1–3 and 9) and aliphatic (entries 5–8) aldehydes, as well as a heteroaromatic aldehyde (entry 10) work well to give the corresponding homoallylic alcohols in good to excellent yields. In the case of a ketone (entry 4), good yields of tertiary alcohols were obtained from the reactions, although the reactions were rather slow compared to the aldehyde cases. It is interesting to note that the catalyst **1** could be filtered after the reaction and recycled more than 20 times without any significant loss of activity in the case of reactions employing aldehydes. However, in the case of the reaction employing acetophenone, somewhat decreased reactivity of the catalyst was observed, giving 70% yields of the product after the third recycle.



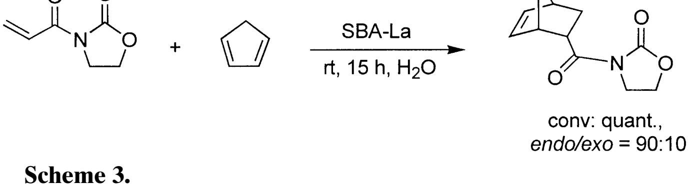
Scheme 2.

Table 1. Catalytic allylation reactions using SBA-La($OTf)_2$ in water.

Entry	R	R^1	Time [h]	Yield [%][a]
1	4-NO_2-C_6H_5	H	6	99 (93[b],95[c])
2	4-OMe-C_6H_5	H	12	90
3	4-Br-C_6H_5	H	8	92
4	C_6H_5	Me	24	90 (70)[d]
5	$C_6H_5CH_2CH_2$	H	8	85
6	cyclo-C_6H_{11}-		12	75
7	C_6H_5CH:CH	H	6	90
8	$CH_3(CH_2)_5$	H	6	93
9	4-Cl-C_6H_5	H	4	98
10	2-Pyridyl	H	8	95

[a] Isolated yield.
[b] From reaction with 0.25 equiv. of tetraallyltin, 24 h;
[c] After 20th recycle.
[d] After 3rd recycle.

Finally we checked the catalytic activity of this catalyst for the Diels–Alder reaction of 3-acryloyl-1,3-oxazolidin-2-one with cyclopentadiene and the reaction also proceeded smoothly in water to afford the corresponding adduct quantitatively (rt, 15 h) as shown in Scheme 3. Control reactions were carried out without the catalyst in aqueous media and no Diels–Alder adduct was obtained at all in the presence or absence of the SBA-15, suggesting the critical role of the lanthanide catalyst.



Scheme 3.

In summary, we have developed a novel mesoporous supported lanthanum catalyst for C−C bond formation reactions in water without using any organic solvents. To the best of our knowledge, this is the first report of the mesoporous material supported Lewis acid catalyst applied in aqueous medium. Simple preparation, easy recovery and reusability of the silica-supported lanthanum catalyst, as well as employment of environmentally benign water as a solvent are expected to contribute to the development of clean technologies.

Experimental Section

Preparation of Catalyst

Preparation of the mesoporous supported lanthanum catalyst was performed according to Scheme 1. The mesoporous material (SBA-15) was synthesized according to the literature procedure.[12] Calcinated SBA-15 (1 g) was treated with 3-(mercapto)propyltrimethoxysilane (5 mL) in dry toluene (10 mL) for 24 h at reflux temperature. The mixture was filtered and extracted for 12 h in CH_2Cl_2/Et_2O mixture using a Soxhlet extractor, then dried under vacuum. The solid material possessing the immobilized mercaptopropyl group was oxidized with H_2O_2 (excess) in methanol (10 mL) for 24 h at rt. After filtration, the mixture was treated with lanthanum(III) chloride (368 mg) in acetonitrile (10 mL) at reflux temperature for 24 h. After cooling to rt, CH_3CN (10 mL) was added and the mixture was filtered and washed with CH_3CN and dried under vacuum to afford the mesoporous supported lanthanum chloride material. Finally, this material was treated with trifluoromethanesulfonic acid (187 mg, 1.24 mmol) in dichloromethane (10 mL) at rt for 12 h. H_2O (10 mL) was added

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and the mixture filtered and washed with H_2O, H_2O-THF, THF, Et_2O and dried under vacuum to afford the catalyst **1**.

Typical Experimental Procedure for the Allylation Reaction

A typical experimental procedure is described for the allylation of acetophenone with tetraallyltin. Acetophenone (0.4 mmol), tetraallyltin (0.2 mmol), and **1** (20 mg, 1.6 mol %) were combined in water (3 mL). The mixture was stirred for 24 h at rt, and solid material was filtered and washed with ethyl acetate. The filtrate was extracted with ethyl acetate, and the combined organic layers were dried ($MgSO_4$). After filtration and concentration, the residue was purified on silica gel chromatography to afford the allylated adduct in 90% yield. The recovered **1** was used directly for the recycling experiments.

Acknowledgements

This work was supported by the Ministry of Science and Technology of Korea through the Research Center for Nanocatalysis, one of the National Science Programs for Key Nanotechnology. P.S. thanks the Brain Korea (BK21) Program for the award of postdoctoral fellowship.

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