

Enantioselective Catalysis over Chiral Imidazolidin-4-one Immobilized on Siliceous and Polymer-Coated Mesocellular Foams

Yugen Zhang,^a Lan Zhao,^a Su Seong Lee,^a and Jackie Y. Ying^{a,*}

^a Institute of Bioengineering and Nanotechnology, 31 Biopolis Way, The Nanos, Singapore 138669, Singapore
Fax: (+65)-6478-9020; e-mail: jyying@ibn.a-star.edu.sg

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Abstract: A highly efficient and enantioselective organocatalyst, imidazolidin-4-one, has been successfully immobilized on siliceous MCF and polymer-coated MCF. The resulting heterogenized catalyst demonstrated excellent catalytic performance and recyclability for Friedel–Crafts alkylation and Diels–Alder cycloaddition. The performance of the supported catalysts in relation to the surface environment of siliceous MCF was examined. It was found that partially pre-capping the MCF with TMS groups enabled us to attain well-dispersed catalysts on the siliceous support with optimal performance. We have also developed a polymer-coated MCF, which retained the porous structure of MCF without the surface silanol groups. High reactivity and excellent recyclability were achieved by the organocatalyst immobilized on polymer-coated MCF.

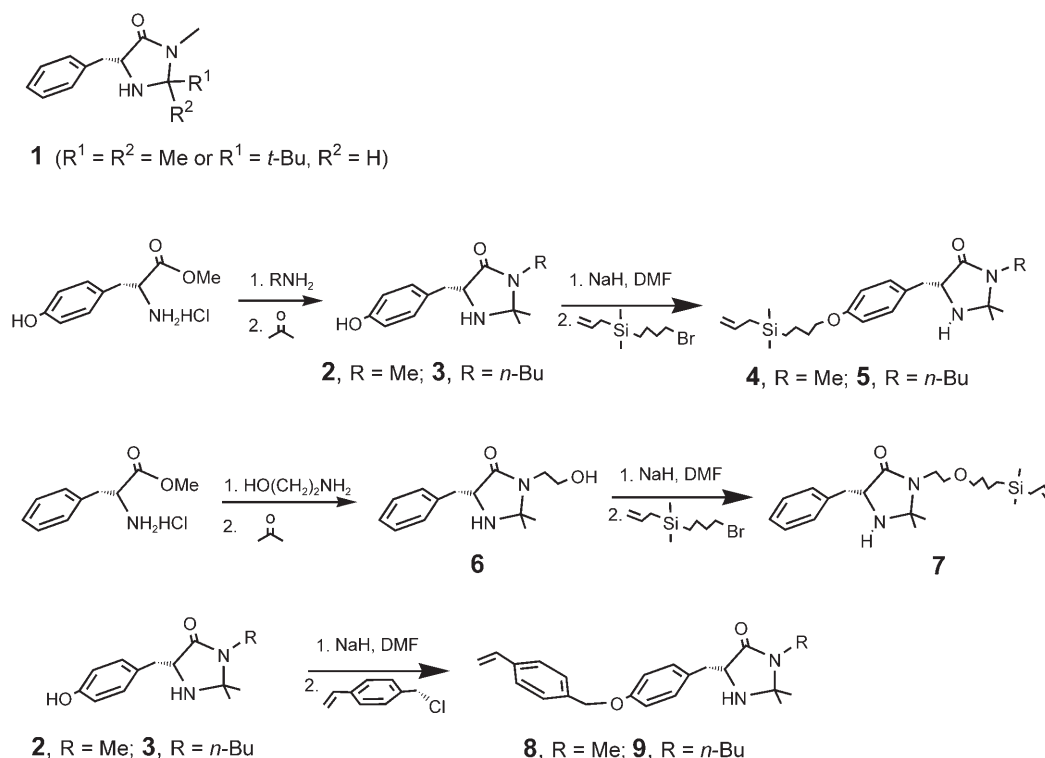
Keywords: heterogeneous catalysis; mesoporous materials; organocatalysis; polymer coating; silica

In the past few years, there has been a tremendous increase in research activities on organic catalysis, especially chiral organic catalysis.^[1] Simple organic molecules could effectively catalyze a variety of fundamentally important transformations, leading to highly enantioselective products.^[1,2] Unlike organometallic catalysts, organic catalysts do not involve metals, giving them greater applicability in the pharmaceuticals industry.^[1c] However, organocatalysts still have some drawbacks, such as the requirement of high catalyst loading, and the difficulty in catalyst separation from the product stream. Solid-supported catalysts might offer the solution to these challenges.^[3] Herein, we report the immobilization of an organocatalyst of high efficiency and enantioselectivity, imidazolidin-4-one, on siliceous mesocellular foam (MCF) and polymer-coated MCF by a novel one-step immobilization

method. This heterogenized catalyst demonstrated excellent catalytic performance and recyclability for Friedel–Crafts alkylation and Diels–Alder cycloaddition. MCF^[4,5] is a novel mesoporous material with unique advantages as a solid support for catalysts. Templated by oil-in-water microemulsions, MCF has a high surface area of 500–800 m²/g, and a 3-dimensional pore structure with ultralarge, cell-like pores (23–42 nm) that are connected by windows of 9–22 nm. Such a pore structure would minimize any steric effects associated with the immobilization of bulky compounds, and facilitate the diffusion of large substrates.

It has been known that the silanol groups on silica surface might affect the activity of the immobilized catalyst.^[5,6] The silanol groups could interact with the active catalytic sites, such as through hydrogen bonding or proton migration in the case of organocatalysts; they could also catalyze certain side-reactions.^[7] In this work, we examined the performance of supported catalysts in relation to the surface environment of siliceous MCF. We have also developed a polymer-coated MCF through the direct radical polymerization of the modified catalyst, cross-linker and vinyl monomer that had been impregnated onto the MCF support.^[8] The polymer-coated MCF retained the MCF pore structure, without the surface silanol groups. High reactivity and excellent recyclability were achieved by the organocatalyst immobilized on polymer-coated MCF.

Imidazolidin-4-one (**1**), one of the key chiral organocatalysts recently developed by MacMillan's group, has been used as an efficient catalyst for a variety of highly enantioselective reactions.^[9,10] It also has great potential for industrial application.^[1c] Therefore, heterogenization of this organocatalyst would be very attractive. Imidazolidin-4-one supported on polymer and silica gel was recently studied for the cycloaddition reactions.^[11] However, the reported chemical efficiency of these heterogenized catalysts was much lower than the homogeneous catalyst.^[11c] Herein, by



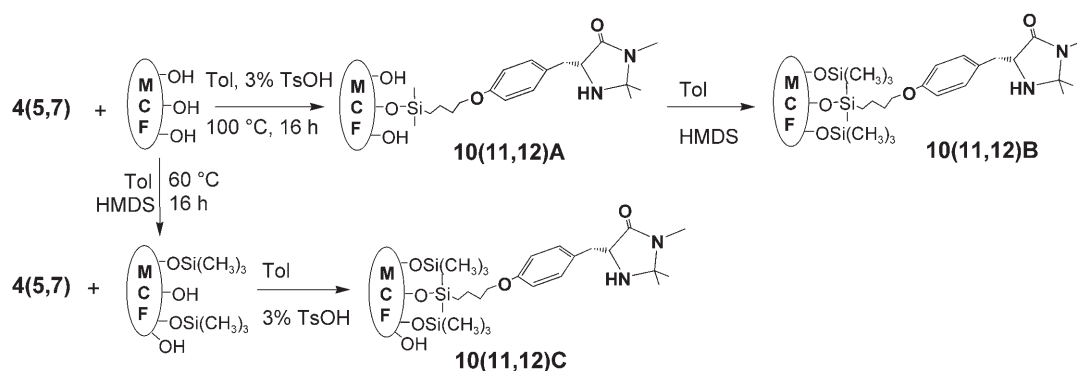
Scheme 1. Synthesis of catalyst precursors.

using the novel siliceous MCF support and the unique immobilization and surface modification schemes, heterogenized catalysts of comparable chemical and stereochemical efficiency as the unsupported imidazolidin-4-one were achieved.

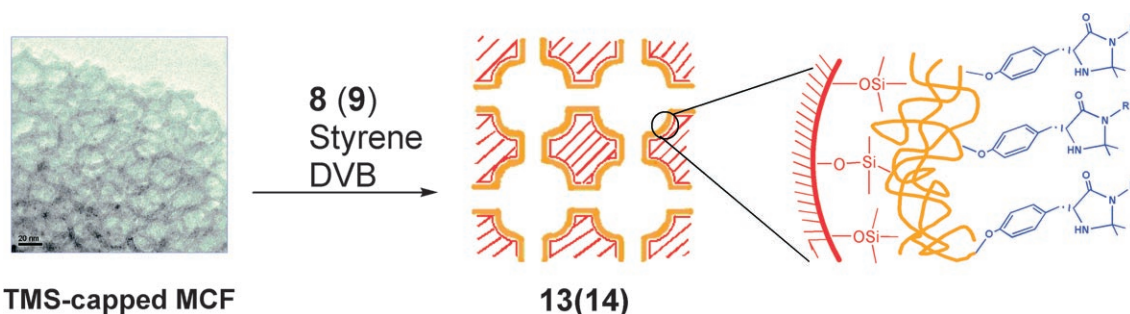
To immobilize the organocatalyst onto MCF, the aryl residue and the amide nitrogen atom of **1** were modified for building different linkages (Scheme 1). The characteristics of the linkages, such as flexibility and length, could be critical to the reactivity of the heterogenized catalysts. Starting from (*S*)-tyrosine methyl ester hydrochloride, the imidazolidinones **2** and **3** were easily obtained in 80–82% yield. On the other hand, (*S*)-phenylalanine reacted with ethanolamine and then acetone to generate imidazolidinone **6**, with the ethylene hydroxy group anchored on the

amide nitrogen. The phenolic group in **2** and **3**, and the hydroxy group in **6** were functionalized by allylsilane^[12] through an *O*-alkylation process to give **4**, **5** and **7**, respectively, in good yields. Finally, **4**, **5**, **7** were anchored onto the surface to generate the supported catalysts **10**, **11** and **12**, respectively (see Scheme 2). By using 3–5% *p*-toluenesulfonic acid (*p*-TsOH) as catalyst, the original allylsilane immobilization method developed by Hayashi's group^[12] was modified and extended to various types of silica supports.^[13] Styrene-modified catalyst monomer **8** or **9** was synthesized by *O*-alkylation of the phenolic group of **2** or **3** with *p*-chloromethylstyrene.

In an effort to examine the relationship between the catalyst performance and the MCF surface environment, heterogenized catalysts **A**, **B** and **C** were de-



Scheme 2. MCF surface modification and catalyst immobilization processes.

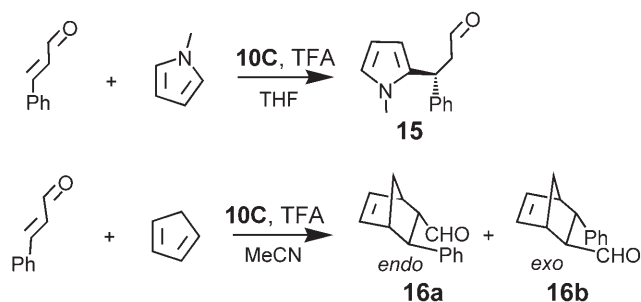


Scheme 3. Synthetic Scheme for catalysts supported on polymer-coated MCF.

veloped with the use of different MCF surface modification schemes (see Scheme 2). In all cases, spherical MCF microparticles of 2–10 μm were used as the support;^[14] they have a BET surface area of 504 m^2/g , a cell-like pore size of 22 nm, and a window size of 13 nm. **A** was obtained from a one-step immobilization onto the MCF support with uncapped silanols. **B** was derived by post-capping of MCF silanols with hexamethyldisilazane (HMDS) after the catalyst immobilization. **C** was attained by immobilizing the catalyst onto an MCF support whose silanols have been partially pre-capped with trimethylsilyl (TMS) groups (0.6–0.8 mmol/g) using a controlled amount of HMDS.

The catalysts supported on polymer-coated MCF, **13** and **14**, were prepared by modifying the method of Ryoo and co-workers.^[8] As illustrated in Scheme 3, MCF was first fully pre-capped with TMS groups by reaction with excess HMDS at 80 °C. Next, styrene-modified catalyst monomer **8** or **9**, styrene, divinylbenzene (DVB) and *a,a'*-azoisobutyronitrile (AIBN) were wet-impregnated onto MCF. The monomers on the pore walls of MCF were directly polymerized by heating to form a uniform polymer-supported catalyst layer on the MCF framework. The catalyst loading, polymer composition and swelling property of this catalyst system could be easily controlled by changing the ratio of different vinyl monomers.

The MCF-supported chiral amine catalysts **A–C** were first studied for the asymmetric Friedel–Crafts alkylation^[15] (see Scheme 4). Prior to this study, there were reports of polymer- and silica-supported imidazolidinone-based catalysts,^[11] but these catalysts were not examined for Friedel–Crafts alkylation. Actually, there has been very little literature on heterogeneous asymmetric Friedel–Crafts alkylation in general.^[16] Table 1 shows that the MCF-supported catalysts were almost similar in reactivity to the unsupported imidazolidinone. However, their enantioselectivity and recyclability strongly depended on the MCF surface modification. Catalyst **10A** gave a good yield at 25 °C, but a lower enantiomeric excess (*ee*) (67%) than the unsupported catalyst (82%).^[9g] This was possibly due to the interaction between the amine groups of the



Scheme 4. Friedel–Crafts alkylation and Diels–Alder cycloaddition reactions.

Table 1. Comparison of catalysts derived from **2** in the synthesis of **15**.

Entry	Catalyst	Run #	Loading (mol %)	TFA	Time [h]	Yield [%] ^[a]	<i>ee</i> [%] ^[b]
1	2	1	20	1	3	78	81
2	2	1	10	1	8	76	82
3	10A ^[c]	1	10	1	6	71	65
4	10A ^[d]	1	10	1	6	72	67
5		2	10	1	5	70	52
6		2 ^[c]	10	0	16	68	60
7		2 ^[c]	10	0.2	8	69	59
8	10B	1	10	1	6	71	68
9		2	10	0.2	8	70	64
10	10C	1	10	1	6	72	74
11		2	10	0.2	8	70	70
12		3	10	0.2	8	69	69
13		4	10	0.2	8	69	68
14	10C ^[f]	1	10	1	72	21	92
15	13	1	10	1	8	72	71
16		2	10	0.2	8	71	71

^[a] Yields based upon isolation of the corresponding alcohol after NaBH_4 reduction.

^[b] Product ratios determined by chiral gas chromatography (GC) (Chiraldex Γ -TA).

^[c] The catalyst loading was 0.20 mmol g^{-1} of MCF.

^[d] The catalyst loading was 0.37 mmol g^{-1} of MCF.

^[e] Second run of a different batch.

^[f] Reaction was run at -30°C .

catalyst with the silanol groups of the uncapped silica surface changing the environment of the catalyst active site. It was found that the catalyst loadings on MCF (0.1–0.4 mmol/g) did not significantly affect the properties of the supported catalysts. The enantioselectivity of **10A** was reduced considerably upon reuse. To retain the activity of the supported catalyst, *ca.* 20% additional trifluoroacetic acid (TFA) should be introduced, to counter the effect of TFA leaching likely during catalyst washes.

Catalyst **10B** was post-capped with TMS groups after the immobilization of **4**. Compared to the uncapped catalyst **10A**, catalyst **10B** showed slightly better enantioselectivity and recyclability (Table 1, entries 8–9). Catalyst **10C**, which was partially pre-capped with TMS prior to the immobilization of **4**, demonstrated superior enantioselectivity and reusability compared to catalysts **10A** and **10B** (see Table 1, entries 10–13). This was likely because the organocatalysts **4** were more well-dispersed throughout the porous support and better separated from each other, when they were loaded onto partially pre-capped MCF support. An *ee* value as high as 92% was achieved with catalyst **10C** when the reaction was run at –30°C (Table 1, entry 14). However, a low yield (21%) was noted even after 72 h, possibly due to the high viscosity of the THF–H₂O solvent mixture at the low temperature.

Besides manipulating the surface chemistry of the MCF support, we also attempted to modify the linkage chemistry of the organocatalyst. For example, the linker group was attached to the amide group (instead of the phenyl group) of **1** in the case of **7** (in contrast to **4** and **5**). Catalyst **7** was found to exhibit a higher enantioselectivity (90%) (Table 2, entry 6) in the homogeneous Friedel–Crafts reaction than the original MacMillan's catalyst^[9] (catalyst **2**) (81%) (Table 1, entry 1). However, its heterogenized counterpart, catalyst **12C**, showed lower activity and significantly reduced enantioselectivity. This showed that the alkyl spacer group attached to the amide nitrogen has some positive impact on the catalytic properties in the homogeneous system, but the linker had adverse effect on the organocatalyst's enantioselectivity when it was involved in the catalyst immobilization onto the MCF support. In contrast, although lower in enantioselectivity than their original homogeneous catalysts (**2** and **3**, respectively), the heterogenized catalysts **10C** and **11C** still demonstrated good enantioselectivities. This suggested that attaching the homogeneous catalysts through a linker group at the phenyl group of **1** would minimize any adverse impact of heterogenizing the organocatalysts for the Friedel–Crafts alkylation reaction.

From the above results, we could conclude that the performance of the MCF-supported imidazolidinone catalysts was greatly dependent on the MCF surface

Table 2. Comparison of catalysts derived from **3** and **7** in the synthesis of **15**.

Entry	Catalyst	Run #	Loading (mol %)	TFA	Time [h]	Yield [%] ^[a]	<i>ee</i> [%] ^[b]
1	3	1	20	1	3	77	80
2	11C	1	10	1	6	72	71
3		2	10	0.2	8	69	65
4	14	1	10	1	8	70	68
5		2	10	0.2	8	70	68
6	7	1	20	1	4	78	90
7	12C	1	10	1	8	60	40

^[a] Yields based upon isolation of the corresponding alcohol after NaBH₄ reduction.

^[b] Determined by chiral GC (Chiraldex Γ -TA).

modification and catalyst linker group. The study illustrated the impact of strong interactions between the silica surface and the catalyst, which could be minimized with the appropriate surface modification scheme. In catalysts **13** and **14**, the MCF surface silanols were fully pre-capped with TMS and coated with polymer. Catalysts **13** and **14** showed similar enantioselectivities as the best MCF-supported catalysts **10C** and **11C** (see Table 1 and Table 2). However, catalysts **13** and **14** demonstrated superior recyclabilities (Table 1, entries 15 and 16; Table 2, entries 4 and 5).

The Diels–Alder cycloaddition reaction (Scheme 4) was also studied to compare the MCF-supported catalysts to the other heterogenized catalysts. Table 3 shows that the MCF-supported catalysts **10C** and **12C** and the polymer-coated MCF-supported catalyst **13** (entries 4, 5, 7–10) provided slightly lower enantioselectivities and similar diastereoselectivities, compared to the polymer- and silica gel-supported catalysts (entries 11–13). However, catalysts **10C**, **12C** and **13** gave the high yields achieved by the homogeneous catalysts (**2** and **7**) with just slightly longer reaction times. In contrast, the polymer- and silica gel-supported catalysts only produced moderate or poor yields even with higher catalyst loading or much longer reaction time. These findings illustrated the benefits of MCF's three-dimensional interconnected pore structure, ultralarge pore size, and high surface area. Organocatalysts were known in many cases to be robust to air and moisture, but sensitive to the presence of acids or bases.^[13,17] Thus, providing a well-controlled catalyst environment *via* a direct one-step catalyst immobilization scheme and an effective support surface modification was critical to the successful development of heterogenized organocatalysts. The issue of support surface modification could be by-passed with the development of polymer-coated MCF.

In conclusion, MCF-supported imidazolidin-4-one catalysts were developed by a direct one-step immobilization process. The MCF surface was carefully modi-

Table 3. Comparison of catalysts derived from **2** and **7**, and polymer-supported and silica gel-supported catalysts in the syntheses of **16a** and **16b**.

Entry	Catalyst	Run #	Loading (mol %)	TFA	Time [h]	Yield [%] ^[a]	exo:endo Ratio ^[b]	ee [%] ^[c]
1	2	1	5	1	24	99	1.3:1	93/93
2	10A	1	5	1	30	93	1.3:1	73/74
3		2	5	0.2	44	96	1.3:1	63/67
4	10C	1	5	1	30	93	1.3:1	83/87
5		2	5	0.2	44	96	1.3:1	76/84
6	7	1	5	1	24	99	1.3:1	91/90
7	12C	1	5	1	30	95	1.3:1	83/85
8		2	5	0.2	44	96	1.3:1	74/80
9	13	1	5	1	35	94	1.3:1	83/86
10		2	5	0.2	44	95	1.3:1	83/86
11	PEG ^[d]	1	10	HBF ₄	-	68	1.3:1	88/-
12	JandaJel ^[e]	1	20	HCl	24	70	1.2:1	99/99
13	Silica gel ^[e]	1	3.3	HCl	64	33	1:1.1	90/90

^[a] Yields based upon isolated product or GC.^[b] Determined by ¹H NMR.^[c] Determined by chiral GC (Chiraldex β-PH).^[d] Refs.^[11a,c]^[e] Ref.^[11b]

fied to modulate the microenvironment of the anchored organocatalysts. The heterogenized catalysts showed high enantioselectivity and activity in both asymmetric Friedel–Crafts alkylation and Diels–Alder cycloaddition reactions. It was important to partially pre-capped the MCF surface with TMS groups to attain separate and well-dispersed catalysts on the siliceous support. Polymer-coated MCF support was also created with immobilized imidazolidin-4-one. This system was free of reactive silanol groups, and provided superior recyclability.

Experimental Section

Synthesis of Catalyst 10C

MCF was dried under vacuum at 180 °C for 16 h. Dry toluene (30 mL) and HMDS (293 mg, 1.8 mmol) were added to the dried MCF (5 g), and the resulting suspension was stirred at 60 °C for 16 h. The mixture was filtered, and the solid was washed successively with methanol, acetone and dichloromethane. After drying under vacuum overnight, the partially TMS-capped MCF (5.26 g) was collected and characterized by IR and elemental analysis (C, H, N). The loading of TMS groups was 0.67 mmol/g based on elemental analysis and weight gain analysis. The modified MCF (5.26 g) was dried under vacuum at 85 °C overnight.

Toluene (30 mL), catalyst precursor **4** (972 mg, 2.5 mmol) and *p*-TsOH (8.5 mg, 0.05 mmol) were then added to the modified MCF sequentially. The suspension was stirred at 100 °C for 24 h. The mixture was then filtered, and the solid was washed thoroughly with methanol, acetone and dichloromethane. After drying under vacuum, catalyst **10C** (5.50 g) was collected and characterized by IR and elemental analysis. The loading of **4** was 0.14 mmol/g based on elemental analysis and weight gain analysis.

Friedel–Crafts Alkylation (Table 1, Entry 10)

MCF-supported catalyst **10C** (0.5 g, 0.07 mmol) was treated with THF (8 mL), H₂O (0.5 mL) and aqueous TFA solution (0.5 M, 140 μL, 0.07 mmol). The mixture was stirred for 10 min, and then *N*-methylpyrrole (310 μL, 3.5 mmol) was added. Next, *trans*-cinnamaldehyde (88 μL, 0.7 mmol) was added dropwise to the reaction vial. The suspension was stirred at room temperature, and the reaction was monitored by thin layer chromatography (TLC). The suspension was centrifuged, and the solution was decanted. This procedure was repeated at least three times using THF as the washing solvent. The solid catalyst was used directly for the next run. The combined solution was prepared following literature procedure^[9g] to give a pure alcoholic product in 72 % yield (108 mg, 0.5 mmol). The ¹H NMR data were in agreement with those reported.^[9g] Enantioselectivity was determined by gas liquid chromatography (GLC) analysis of the corresponding aldehyde (Chiraldex Γ-TA column, 30 m × 0.25 mm I.D., 5 °C min⁻¹ ramp from 70 °C to 170 °C, 23 psi); *R* isomer: *t*_r = 26.6 min, and *S* isomer: *t*_r = 27.4 min.^[9g]

See Supporting Information for other experimental details.

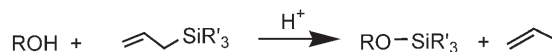
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