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Mesoporous aluminosilicate-catalyzed allylation of aldehydes with allylsilanes

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ABSTRACT

Mesoporous aluminosilicate (Al-MCM-41) was found to catalyze the allylation of both aromatic and aliphatic aldehydes with allylsilanes although amorphous silica–alumina or mesoporous silicates (MCM-41, SBA-15) could not catalyze the reaction under the same reaction conditions. The solid acid catalyst Al-MCM-41 could be reused three times without significant loss of activity.

Among a wide variety of carbon–carbon bond forming reactions, the addition of allylsilanes to aldehydes is one of the useful reactions. Typically, these reactions are performed under stoichiometric or near-stoichiometric amounts of strong Lewis acids (e.g., $TiCl_4$, $BF_3{\cdot}OEt_2$, and $AlCl_3$).[1,2] Many kinds of catalysts, such as $Sc(OTf)_3$,[3] $Yb(OTf)_3$,[4] iodine,[5] and $FeCl_3$,[6] are also known to promote this transformation. However, the catalyst separation and recycling are difficult for these homogeneous systems.

Owing to the economic and environmental considerations, there has been increasing attention to the heterogeneous organic reactions catalyzed by solid acid catalysts.[7–9] Although some heterogeneous catalysts (metal cations or proton-exchanged montmorillonites[10,11] and rare earth metals exchanged zeolite-Y[12]) have been investigated for the reaction of aldehydes with allylsilanes, these catalytic systems sometimes have disadvantages such as higher reaction temperature or low yields of the allylated products.

On the other hand, mesoporous aluminosilicate, Al-MCM-41, is well known to show remarkable acidic properties. Since its pore sizes are larger than those of zeolites, bulky organic substrates can contact acid sites of mesoporous aluminosilicates. Therefore, Al-MCM-41 has been shown to catalyze several organic transformations.[13–19] However, most of these reactions are vapor phase or high-temperature reactions,[13–17] and there has been relatively few reports on the synthetic application of Al-MCM-41 as a solid acid catalyst for liquid-phase reactions under mild reaction conditions.[18,19] Herein, we report the facile catalytic system for the reaction of aldehydes with allylsilanes by using Al-MCM-41.

Al-MCM-41 (Si/Al = 26) was synthesized by a known procedure with slight modification,[20,21] and was used after drying at 120 °C for 1 h under vacuum. First, the effect of solvent was examined for the reaction of benzaldehyde (1.0 mmol) and allyltrimethylsilane (1.5 mmol) in the presence of Al-MCM-41 (30 mg). The best result was obtained when the reaction was carried out in dichloromethane at 15 °C for 2.5 h, and the corresponding homoallyl silyl ether was isolated in 93% yield after filtration of the catalyst, concentration of the filtrate, and the purification by silica-gel column chromatography (Table 1, entry 1). The use of toluene or nitromethane as a solvent also afforded the homoallyl silyl ether in almost same yields (entries 2 and 3). The reaction did not take place in ether, THF, cyclohexane, or hexane (entries 4–7). Next, the reaction was performed in the presence of amorphous silica–alumina (JRC-SAH-1, JRC-SAL-2)[22] in dichloromethane at 15 °C. In both cases, the reaction did not proceed (entries 8 and 9). Furthermore, benzaldehyde was not reacted in the presence of aluminium-free MCM-41 or SBA-15 (entries 10 and 11). These results suggest that both mesoporous structure and the presence of aluminium moiety are necessary for the catalytic activity of Al-MCM-41. When the reaction was performed in dichloromethane at 30 °C, the reaction was completed after 1 h and the corresponding homoallyl silyl ether was obtained in 92% yield (entry 12).[23]

Then the Al-MCM-41-catalyzed allylation was applied to various aldehydes. The results are summarized in Table 2. Aromatic aldehydes bearing electron-withdrawing groups were quickly allylated within 30 min in excellent yields (entries 1–6). *o*-, *m*-, and *p*-Tolualdehyde, bearing electron-donating alkyl substituent, was less reactive than benzaldehyde and the allylated products were obtained in moderate to good yields (entries 7–9), whereas *p*-anisaldehyde gave only trace amount of the product (entry 10). Although the reactivities of naphthaldehydes were also lower than that of benzaldehyde, the corresponding homoallyl silyl ethers were obtained in good yields (entries 11–14). Aromatic aldehydes

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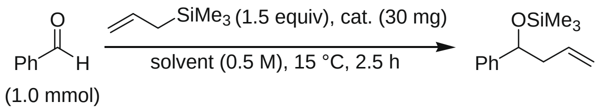
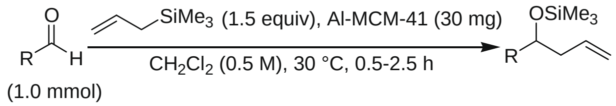
Table 1
Allylation of benzaldehyde with allyltrimethylsilane



Entry	Cat.	Solvent	Yield[a] (%)
1	Al-MCM-41	CH_2Cl_2	93
2	Al-MCM-41	Toluene	87
3	Al-MCM-41	$MeNO_2$	85
4	Al-MCM-41	Et_2O	N.R.
5	Al-MCM-41	THF	N.R.
6	Al-MCM-41	Cyclohexane	N.R.
7	Al-MCM-41	Hexane	N.R.
8	JRC-SAH-1[b]	CH_2Cl_2	N.R.
9	JRC-SAL-2[c]	CH_2Cl_2	N.R.
10	MCM-41	CH_2Cl_2	N.R.
11	SBA-15	CH_2Cl_2	N.R.
12[d]	Al-MCM-41	CH_2Cl_2	92

[a] Isolated yield after column chromatography.
[b] Amorphous silica alumina (Si/Al = 2).
[c] Amorphous silica alumina (Si/Al = 5).
[d] Reaction was performed at 30 °C for 1 h.

Table 2
Allylation of various aldehydes with allyltrimethylsilane catalyzed by Al-MCM-41



Entry	R	Time (h)	Yield[a] (%)
1	$4\text{-}NO_2C_6H_4$	0.5	92
2	$4\text{-}BrC_6H_4$	0.5	97
3	$4\text{-}ClC_6H_4$	0.5	93
4	$2\text{-}NO_2C_6H_4$	0.5	90
5	$2\text{-}BrC_6H_4$	0.5	95
6	$2\text{-}ClC_6H_4$	0.5	93
7[b]	$4\text{-}MeC_6H_4$	2.5	59
8	$3\text{-}MeC_6H_4$	1	70
9	$2\text{-}MeC_6H_4$	1	83
10	$4\text{-}MeOC_6H_4$	1	<3
11	2-Naphtyl	1	70
12[b]	2-Naphtyl	1	74
13	1-Naphtyl	1	61
14[b]	1-Naphtyl	1	67
15	$PhCH_2CH_2$	1	26[c] (20)[d]
16[b]	$PhCH_2CH_2$	1	60[c] (48)[d]
17	$c\text{-}C_6H_{11}$	1	54[c] (44)[d]
18[b]	$c\text{-}C_6H_{11}$	1	86[c] (73)[d]
19	*t*-Bu	1	85

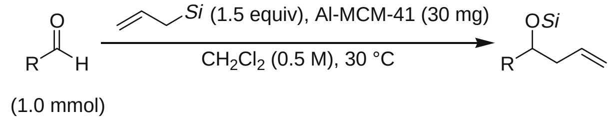
[a] Isolated yield after column chromatography unless otherwise noted.
[b] Al-MCM-41 (50 mg) was used.
[c] Determined by ^1H NMR analysis using nitromethane as an internal standard.
[d] Isolated yield of the corresponding homoallylalcohol after hydrolysis.

Table 3
Reuse of Al-MCM-41[a]

Run	$4\text{-}NO_2C_6H_4CHO$ (mmol)	Al-MCM-41 (mg)	Yield[b] (%)
1	2.0	60	92
2	1.8	53	94
3	1.3	38	94
4	0.8	25	93

[a] In the presence of Al-MCM-41 (30 mg/mmol), the reaction of 4-nitrobenzaldehyde with 1.5 equiv of allyltrimethylsilane was carried out in dichloromethane (0.5 M) at 30 °C for 0.5 h.
[b] Isolated yield after column chromatography.

Table 4
Allylation of aldehydes with various allylsilanes catalyzed by Al-MCM-41



Entry	R	*Si*[a]	Time (h)	Yield[b] (%)
1	$4\text{-}NO_2C_6H_4$	TES	0.5	93
2	$4\text{-}NO_2C_6H_4$	TBDMS	0.5	91
3	$4\text{-}NO_2C_6H_4$	TBDPS	0.5	57[c]
4	Ph	TBDMS	1	86
5	*t*-Bu	TBDMS	1	87

[a] TES = triethylsilyl, TBDMS = *tert*-butyldimethylsilyl, TBDPS = *tert*-butyldiphenylsilyl.
[b] Isolated yield after column chromatography.
[c] Al-MCM-41 (50 mg) was used.

are often diallylated by Lewis acid-catalyzed allylation.[6] However, the diallylated product was not detected in this catalytic system. The reaction of aliphatic aldehydes was also examined. In the case of 3-phenylpropanal and cyclohexanecarboxaldehyde, the formation of the corresponding silyl enol ethers caused the decrease of the yield of the allylated products (entries 15 and 17). The yields were improved by increasing the amount of the catalyst (entries 16 and 18). Pivalaldehyde was allylated in 85% yield despite its steric hindrance (entry 19). The reaction of acetophenone with allyltrimethylsilane did not occur and the corresponding self-aldol adduct was obtained in low yield under the same reaction conditions given in Table 2.

The recovery and reuse of the catalyst were also examined. After the reaction of 4-nitrobenzaldehyde with allyltrimethylsilane, Al-MCM-41 was recovered by filtration. Then, the recovered catalyst was dried at 70 °C for 15 min and treated in the same manner as the first run. The catalyst could be reused three times without significant loss of catalytic activity (Table 3).

In terms of synthetic application, bulkier silyl ethers are often useful for the protective groups of alcohols than trimethylsilyl ether. Then, the reaction of aldehydes with other allylsilanes was examined. 4-Nitrobenzaldehyde was allylated quickly with allyltriethylsilane or allyl*tert*-butyldimethylsilane under the same reaction conditions given in Table 2. The corresponding homoallyl silyl ethers were obtained in 93% and 91% yields, respectively (Table 4, entries 1 and 2). Probably because of the steric hindrance, the reaction of 4-nitrobenzaldehyde with allyl*tert*-butyldiphenylsilane afforded desired product only in moderate yield even using increased amount of the catalyst (entry 3). Benzaldehyde and pivalaldehyde were also allylated with allyl*tert*-butyldimethylsilane in 86% and 87% yields, respectively (entries 4 and 5).

In conclusion, allylation of various aldehydes with allylsilanes was promoted under mild reaction conditions by using Al-MCM-41 as a solid acid catalyst to afford the corresponding silyl ethers. The superiority of Al-MCM-41 over amorphous silica–alumina is probably due to more efficient interaction between organic substrate and solid surface caused by concentration effect inside the ordered, hydrophobic mesopores with high-surface area. The recovered Al-MCM-41 could be reused three times without any decrease in catalytic activity.

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21. The specific surface area (BET) and the average pore diameter (BJH) were 1120 m^2/g and 2.7 nm, respectively.
22. Reference catalysts from the Catalysis Society of Japan. The specific surface areas (BET) of JRC-SAH-1 and JRC-SAL-2 were 610 m^2/g and 570 m^2/g, respectively.
23. *Typical experimental procedure*: Under an atmosphere of argon, to a mixture of benzaldehyde (0.106 g, 1.0 mmol) and Al-MCM-41 (30 mg, dried prior to use at 120 °C for 1 h under vacuum) in dichloromethane (1.5 mL), allyltrimethylsilane (0.172 g, 1.5 mmol) in dichloromethane (0.5 mL) was added through a syringe at 30 °C. The reaction mixture was stirred at 30 °C for 1 h and the catalyst was removed by filtration. After the filtrate was concentrated under reduced pressure, almost pure homoallyl silyl ether was obtained. Further purification by silica-gel column chromatography (hexane/Et_2O = 20:1) afforded 4-trimethylsiloxy-4-phenyl-1-butene[24] as a colorless oil (0.203 g, 92%). The product gave satisfactory IR and ^1H, ^{13}C NMR spectra.
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