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Cesium Carbonate Supported on Alumina for the Michael Addition of Diethyl Malonate to Methyl Acrylates

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The cesium salts supported on γ-Al_2O_3 were highly active catalysts for the Michael addition of diethyl malonate (**1**) to methyl acrylate (**2**) in toluene as solvent. The use of a limited amount of **2** gave diethyl [2-(methoxycarbonyl)ethyl]-malonate (**3**), however the formation of diethyl bis[2-(methoxycarbonyl)ethyl]malonate (**4**) was enhanced by the increase in amounts of **2**. Catalytic activities were easily recovered by the calcination of used catalysts. IR and XRD observations indicate that the active catalytic species are Cs_2CO_3 on Al_2O_3. The use of malononitrile enhanced the formation of the diadduct as principal products by addition to methyl acrylate. Other methyl acrylates, such as methyl methacrylate and methyl crotonate, gave low yield of the products.

Base-catalyzed reactions, such as Michael, Knoevenagel, and aldol reactions, esterification of carboxylic acid with alcohol, transesterification of fatty oils with alcohol, and isomerization of olefins, are important for academic research and industrial production.[1–3] Although homogeneous bases are widely used catalysts for these reactions, separation of the catalysts from the reaction mixtures presents a particularly energy demanding high environmental burden. Thus, heterogeneous catalytic processes are anticipated to resolve the burden.[4–14] They involve base catalysts, such as alkali hydroxides, carbonates, and fluorides, and alkaline earth metal oxide by themselves or on appropriate inorganic support. Recently, there have been some reports of organo-functionalized mesoporous materials.[15–23] We also have found mesoporous materials with SDA for typical base-catalyzed reactions, such as the Michael, Knoevenagel, and aldol reactions.[24] However, these organo-functionalized catalysts show some instability due to leaching of organo-moieties from the catalysts. We have been interested in alkaline salts, such as sodium, potassium, and cesium, particularly cesium salts, for these base-catalyzed reactions.[25–37] There have been some attempts at cesium catalysts in mesoporous arrays, however they have not given successful results because the cesium destroys the mesoporous array during the preparation of cesium-loaded catalysts on mesoporous materials, particularly MCM-41 materials.[25–29]

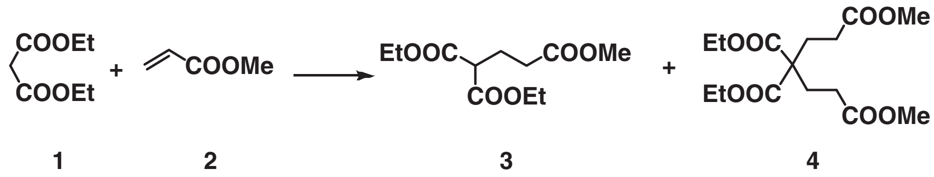
During the efforts to explore stable base catalysts, we have found that Cs_2CO_3 supported on Al_2O_3 gives excellent results for some base-catalyzed reactions, such as Michael addition and dimerization of glycerine.[38] In this work, we focused on cesium loaded on γ-Al_2O_3 in the Michael addition of diethyl malonate (**1**) as a donor to methyl acrylate (**2**) as an acceptor (Scheme 1). The Michael addition of active methylene compounds to other methyl acrylates have also been examined over Cs_2CO_3/Al_2O_3 catalysts.

Experimental

Preparation of Cesium Salts Supported on Alumina. Ce_2CO_3, CsOAc, and $CsNO_3$ were obtained commercially from Nakalai Tesque, Kyoto, Japan. γ-Alumina (N-610; JGC C&C, Kawasaki, Japan) was used as Al_2O_3 source. Typical catalyst preparation for Cs_2CO_3/Al_2O_3 is as follows: Al_2O_3 (2.0 g) and Cs_2CO_3 (1.15 g (6 mmol); Kanto Chem. Co., Inc., Tokyo, Japan) were suspended in 20 mL of methanol, and stirred for 2 h at room temperature. Methanol was removed in vacuo at 35 °C, and dried at 40 °C overnight. The resulting catalyst was heated to 450 °C with a programmed rate of 1 °C min^{-1}, and kept 6 h at 450 °C. The loading of other salts was done similarly. The calcination at 700 °C was carried out in a similar method as at 450 °C.

The amount of cesium was based on the weight of elemental cesium relative to the weight of solid support. Charcoal and silica gel were obtained from Nakalai Tesque, Kyoto, Japan. MCM-41 was prepared according to the literature.[39]

Michael Addition of Diethyl Malonate to Methyl Acrylate. Typical reaction was carried out using diethyl malonate (**1**; 1.0 mmol; Aldrich, Tokyo, Japan) and methyl



Scheme 1.

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Table 1. Effects of Support of Cs_2CO_3 on the Activity and the Selectivity for the Michael Addition of Diethyl Malonate to Methyl Acrylate[a)]

Support	Conversion /%	Yield (Selectivity)[b)]/%	
		3	4
None	98	83 (87)	13 (13)
Al_2O_3	93	77 (83)	17 (10)
MCM-41	4	4 (100)	0 (0)
SiO_2	8	8 (100)	0 (0)
Charcoal	33	33 (99)	0.3 (1)
KF[c)]	91	77 (85)	14 (15)

a) Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst (loaded 30 wt % cesium on the support, and calcined at 450 °C for 6 h): 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **3** and **4** are shown in parentheses. c) KF/Al_2O_3 (30 wt % KF on Al_2O_3).

acrylate (**2**; 1.2 mmol; Nakalai Tesque, Kyoto, Japan) in the presence of the catalyst (100 mg) for 4 h at 80 °C using toluene as solvent. The conversion and selectivity for diethyl [2-(methoxycarbonyl)ethyl]malonate (**3**) and diethyl bis[2-(methoxycarbonyl)ethyl]malonate (**4**) were determined on a Shimadzu GC-18A Gas chromatograph equipped with a TC-17 column (30 m × 0.25 mm × 0.25 µm, GL Science Inc., Tokyo, Japan). The chemical structures of **3** and **4** were determined by ^1H NMR spectroscopy on a Varian Inova 400 spectrometer after purification by column chromatography using hexane/EtOAc (10/1) as an eluent. The products were also confirmed on a Shimadzu GCMS-QP5000 Gas chromatograph-Mass spectrometer. The yield and selectivity of adducts were calculated on the basis of the amount of donor **1** introduced and consumed, respectively. The Michael reactions using other substrate were carried out in the same ways as the reactions of **1** and **2**.

Recycling of the Catalysts. Recycling of the used catalysts was carried out after filtration of products and washing well with toluene. Resulting catalyst was calcined at 450 °C for 6 h. The reactions were carried out in the same conditions as the first reaction.

Characterization of Catalysts. Powder X-ray diffraction (XRD) was recorded on a Shimadzu XRD-6000 diffractometer with Cu Kα radiation ($\alpha = 1.5418$ Å). FT-IR spectra were measured by KBr method using Nexus 470, Thermo Electron, MA, USA. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a Shimadzu Thermogravimetric Analyzer DTG-50A with a temperature programmed rate of 10 °C min^{-1} in an air flow.

Results and Discussion

Effects of Support for Cs_2CO_3. Table 1 shows effects of the support for Cs_2CO_3 on the Michael addition of **1** to **2**. Al_2O_3, itself, had no catalytic activity, however Cs_2CO_3 supported on Al_2O_3 appeared high activity for the reaction. **3** (monoadduct) was a principal product by the first step reaction of **1** with **2**, accompanying small amounts of **4** (diadduct) by the second step reaction of **3** with **2**. Charcoal gave moderately activity, however silica supports, MCM-41 and silica gel, had only low activities. 30 wt % KF/Al_2O_3, which has one of the highest activities, had similar level activity to 30 wt % Cs_2CO_3/Al_2O_3.[12,13]

Table 2. Effects of Cesium Precursor and Calcination of Cesium Salt Supported on Al_2O_3 on the Activity and Selectivity for the Michael Addition of Diethyl Malonate to Methyl Acrylate[a)]

	Calcination /°C	Conversion /%	Yield (Selectivity)[b)]/%	
			3	4
Cs_2CO_3	—[c)]	95	79 (83)	16 (17)
	450	93	77 (83)	16 (17)
	700	75	68 (90)	7 (10)
CsOAc	—[c)]	35	35 (99)	0.3 (1)
	450	94	73 (78)	21 (22)
$CsNO_3$	—[c)]	0	—	—
	450	8	8 (100)	0 (0)
	700	76	68 (89)	8 (11)

a) Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst: 30 wt % Cs/Al_2O_3 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **3** and **4** are shown in parentheses. c) Dried at 40 °C.

Mesoporous arrays of MCM-41 were destroyed by the loading of Cs_2CO_3 as shown in Figures S1 and S2 in Supporting Information. Kloetstra et al. and Ernst et al. described the decay of mesoporous arrays of MCM-41 by cesium loading.[25–27] Resulting catalysts were modestly active for the Michael addition of **1** to **2** although high activities were described for Knoevenagel reaction of benzaldehyde with ethyl cyanoacetate or malononitrile,[25,27] and for the Michael addition of diethyl malonate (**1**) to neopentyl glycol diacrylate.[26]

Cs_2CO_3, itself, had high activity corresponding to 30 wt % Cs_2CO_3/Al_2O_3. However, it was difficult to separate the catalyst and product solution by filtration, because the solution was colloidal after the reaction. Loading of Cs_2CO_3 on Al_2O_3 is a promising way for the separation of the catalysts from the products (see also recycling section).

Effects of Types of Cesium Salt. Table 2 shows typical results of three types of cesium salts supported on Al_2O_3 for the Michael addtion of **1** to **2**. 30 wt % Cs_2CO_3/Al_2O_3 gave high conversion of both of the samples dried at 40 °C and calcined at 450 °C. Catalytic activity of 30 wt % $CsOAc/Al_2O_3$ dried at 40 °C remained 35%, however the activity was enhanced after the calcination at 450 °C. On the other hand, 30 wt % $CsNO_3/Al_2O_3$ has almost no activity using a sample dried at 40 °C. The calcination of 30 wt % $CsNO_3/Al_2O_3$ at 450 °C gave only low activity, however reasonable activity appeared after the calcination at 700 °C. These differences are due to the active species formed by the calcination. Detailed discussion on the differences will be given in the later sections. We adopted Cs_2CO_3 supported on Al_2O_3 after the calcination at 450 °C for further studies of the Michael additions.

Effects of Reaction Temperature. Figure 1 shows effects of reaction temperature on the Michael addition of **1** to **2** over 30 wt % Cs_2CO_3/Al_2O_3. The reaction occurred even at 25°C in low conversion, and enhanced rapidly with an increase in the temperature.

3 was an only product at low temperature, however the formation of **4** was increased with the increase in the

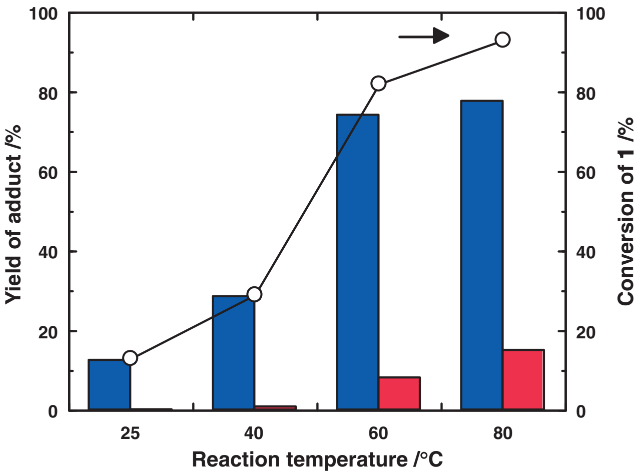


Figure 1. Effects of reaction temperature on the product in the Michael addition of diethyl malonate to methyl acrylate. Reaction conditions: **1**: 1.2 mmol; **2**: 1.0 mmol; catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene, 4 mL; temperature: 25–80 °C; period: 6 h. Legend: 🟦: **3**; 🟥: **4**.

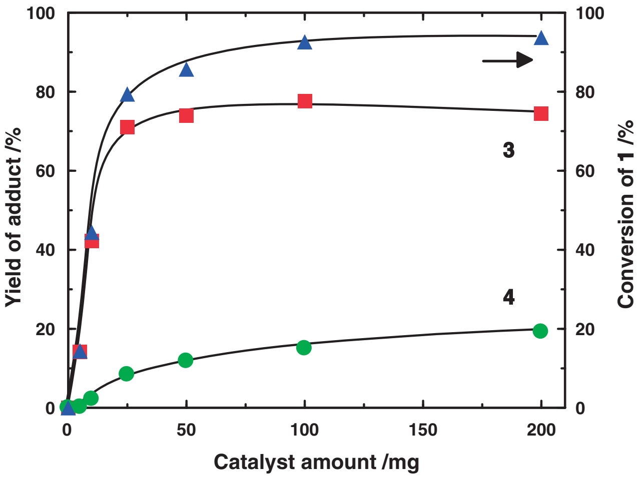


Figure 2. Effects of catalyst amount on the product in the Michael addition of diethyl malonate to methyl acrylate. Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 0–200 mg; solvent: toluene, 4 mL; temperature: 80 °C; period: 6 h.

Table 3. Effects of Cs_2CO_3 Supported on Al_2O_3 in the Michael Addition of Diethyl Malonate to Methyl Acrylate Using the Same Weight of Catalyst[a)]

Loading Cs_2CO_3 /wt%	Conversion /%	Yield (Selectivity)[b)]/% **3**	**4**
0	0	—	—
10	14	14 (99)	0.1 (1)
15	46	44 (95)	2 (5)
20	83	71 (86)	12 (14)
30	94	70 (74)	24 (26)
50	92	75 (81)	17 (19)

a) Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst: 0–50 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **3** and **4** are shown in parentheses.

Table 4. Effects of Loading Amount of Cs_2CO_3 Supported on Al_2O_3 in the Michael Addition of Diethyl Malonate to Methyl Acrylate by Using the Same Amount of Cs_2CO_3[a)]

Loading Cs_2CO_3 /wt%	Catalyst /mg	Conversion /%	Yield (Selectivity)[b)]/% **3**	**4**
10	300	21	21 (99)	0.2 (1)
15	200	38	37 (98)	1 (2)
20	150	89	72 (81)	17 (19)
30	100	93	77 (83)	16 (17)
50	60	90	74 (82)	16 (18)

a) Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **3** and **4** are shown in parentheses.

temperature. A similar increase in catalytic activity was also observed for unsupported Cs_2CO_3. From these observations, we adopted 80 °C as the standard reaction temperature.

Effects of Cesium Amount. Figure 2 shows effects of amount of 30 wt% Cs_2CO_3/Al_2O_3 on the activity and yield of **3** and **4**. The Michael addition did not occur in the absence of 30 wt% Cs_2CO_3/Al_2O_3. Catalytic activity was enhanced by the increase in the catalyst amount, however then, gradually saturated with the further increase.

The yield of **3** also rapidly reached 60%, and saturated with further increase, however the yield of **4** increased gradually with the increase in the catalyst amount.

Table 3 shows effects of the loading of Cs_2CO_3 on catalytic activity for the Michael addition, where the cesium amount remained 30 mg. The catalytic activity was low for 10 and 15 wt% Cs_2CO_3/Al_2O_3, however the catalytic activity increased with the increase in the loading to 20–50 wt%. These results mean the dispersion of Cs_2CO_3 on Al_2O_3 highly influenced the catalytic activity.

3 was an only product at the low loadings, however the higher loadings of Cs_2CO_3 increased the formation of **4**. These results indicate that the second step reaction of **3** to **4** was more rapid than that of **1** to **3**.

Table 4 summarizes effects of the catalyst loaded Cs_2CO_3 on Al_2O_3 on catalytic activity for the Michael addition of **1** to **2**. The activities were increased by the increase in the loading of Cs_2CO_3 (by using the same weights of the catalysts), and then saturated by the further increase in the loading of Cs_2CO_3.

The yield of **3** was saturated with the increase in the loading of Cs_2CO_3, however the formation of **4** increased gradually.

The data shown in Tables 3 and 4 indicate the highly dispersed Cs_2CO_3 on Al_2O_3 is not highly active even if the same of amounts of cesium are used in the reaction. However, 20 wt% Cs_2CO_3/Al_2O_3 is essential for high catalyst performance. These results mean that high loadings of Cs_2CO_3 are important for the Michael addition, and that the bulk cesium species have higher activities than the highly dispersed cesium species. From these observations, we decided 30 wt% Cs_2CO_3/Al_2O_3 as a standard loading for further studies.

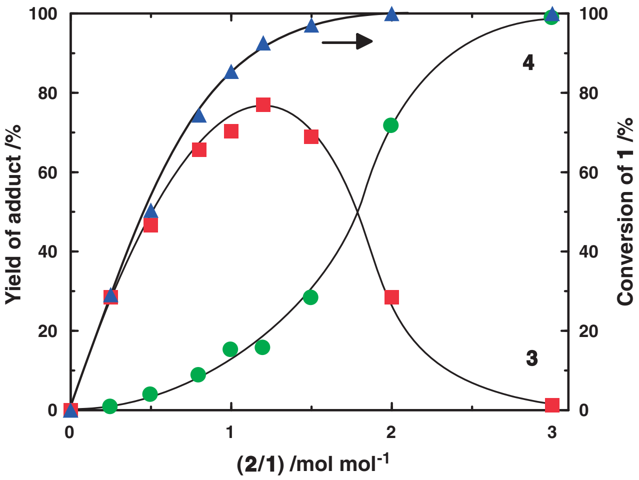


Figure 3. Effects of ratio of methyl acrylate to diethyl malonate in the Michael addition. Reaction conditions: **1**: 1.0 mmol; **2**: 0.25–3.0 mmol; catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene, 4 mL; temperature: 80 °C; period: 6 h.

Effects of the Ratio of Methyl Acrylate to Diethyl Malonate. Figure 3 shows effects of the ratio of **2** to **1** on the Michael addition over 30 wt% Cs_2CO_3/Al_2O_3. The conversion of **1** was increased with the increase in the ratio. The monoadduct **3** was predominant over the diadduct **4** at the low ratios, however the formation of **4** was rapidly enhanced with the increase in the ratio. Further, the formation of **4** exclusively occurred at the ratio of 3.0. These results mean that the second step of **3** to **4** was highly enhanced in the presence of excess of **2**.

Recycling of Cs_2CO_3/Al_2O_3 Catalyst. Figure 4 shows the recycling of the 30 wt% Cs_2CO_3/Al_2O_3 catalysts used for the Michael addition. The catalytic activity was decreased by first and second recycles of the used catalysts after washing with toluene. However, the catalytic activity was easily recovered by the calcination of the third recycled catalyst. This means that the decreases in catalytic activity in first and second recycles were not due to leaching of the cesium species, however the catalysts were deactivated by the accumulation of organic molecules on cesium species because catalytic activity was recovered by the calcination of the third recycled catalyst.

Figure 5 shows the TGA and DTA profiles of the used 30 wt% Cs_2CO_3/Al_2O_3 catalysts in an air stream. Significant weight losses were found in the range of 200 to 400 °C. The exothermic changes were also observed in the corresponding ranges. These results mean that the organic moieties were accumulated on the catalyst during the reaction, resulting in the decrease in catalytic activity by recycling. The catalytic activity of Cs_2CO_3 is recovered by calcination of the recycled catalyst due to removal of organic moieties. This is one of the advantages of using Cs_2CO_3.

Michael Addition of Other Substrates. Table 5 shows the Michael addition of some donor nucleophiles **5** to **2** over 30 wt% Cs_2CO_3/Al_2O_3. All donors predominantly gave monoadduct by the use of 1.2 equivalents of **2** to **5**. However, the formation of diadduct was enhanced in the presence of 2.0 equivalents of **2** to **5**. Particularly, donors with cyano-moiety, a strong electron-withdrawing group, gave the diadduct **7** selectively. Diethyl and di-*n*-butyl malonates also gave the diadduct predominantly, however the di-*t*-butyl malonate with bulky groups selectively gave monoadduct **6** even in the presence of 2 equivalents of **5**. These results mean that the electron-withdrawing groups of the donors enhance the Michael addition as in previous literature,[1,3] and that the reaction was highly influenced by the steric hindrance of the donors.

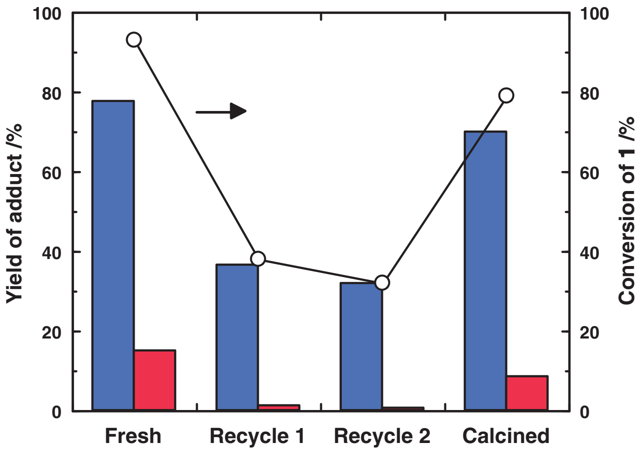


Figure 4. Recycling of Cs_2CO_3/Al_2O_3 catalysts. Reaction conditions: **1**: 1.0 mmol; **2**: 1.2 mmol; catalyst (fresh): 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene, 4 mL; temperature: 80 °C; period: 6 h. Legends: see Figure 1.

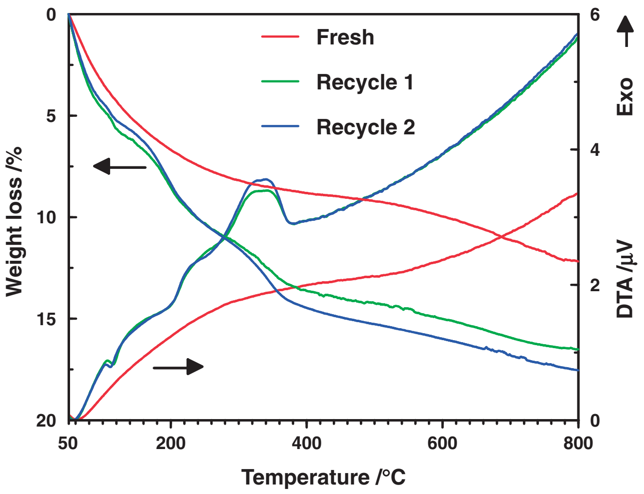
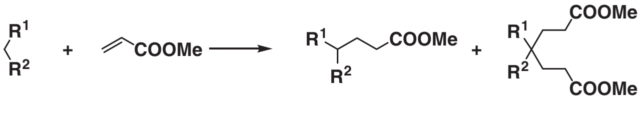


Figure 5. TGA and DTA profiles of recycled catalysts. Reaction conditions: see Figure 4.

Table 6 summarizes the Michael addition of α,β-unsaturated carboxylates **9** with donors **8**, such as **1** and malononitrile, over 30 wt% Cs_2CO_3/Al_2O_3 in the presence of 2.0 equivalents of **9** to **8**. The addition of **8** to **9** gave principally diadducts **11**. The selectivity for **10** with malononitrile as a donor was higher than that with **1** probably due to high nucleophilicity by electron-withdrawing CN moieties. The addition of **8** to the sterically hindered methyl methacrylate and methyl crotonate, gave only low activities, resulting in selective formation of monoadduct **10** even in excess of **9**. Vinyl acetate and styrene were inactive for the donors **8** (not shown in Table 6).

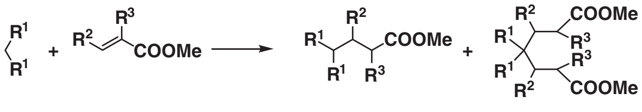
Table 5. Effects of Substitution of Active Methylene Compounds on the Michael Addition to Methyl Acrylate[a)]

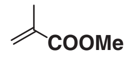


R^1 R^2	2/5 /mol mol^{-1}	Conversion /%	Yield (Selectivity)$^{b)}$/% 6	7
CN CN	1.2	84	62 (74)	22 (26)
	2.0	100	0 (0)	100 (100)
CN COOEt	1.2	71	24 (34)	47 (66)
	2.0	99	1 (1)	99 (99)
CN COO-*t*-Bu	1.2	79	41 (52)	38 (48)
	2.0	99	11 (11)	89 (89)
COOEt COOEt	1.2	93	77 (83)	16 (17)
	2.0	100	28 (28)	72 (72)
COO-*n*-Bu COO-*n*-Bu	1.2	91	73 (80)	18 (20)
	2.0	100	26 (26)	74 (74)
COO-*t*-Bu COO-*t*-Bu	1.2	48	47 (97)	1 (3)
	2.0	82	80 (98)	2 (2)
CN Ph	1.2	31	23 (75)	8 (25)
	2.0	37	27 (73)	10 (27)

a) Reaction conditions: **5**: 1.0 mmol; **2**: 1.2 or 2.0 mmol, catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **6** and **7** are shown in parentheses.

Table 6. Effects of Substitution of Methyl α,β-Unsaturated Carboxylates on the Michael Addition of Diethyl Malonate and Malononitrile[a)]



R^1 R^1	R^2, R^3, COOMe	Conversion /%	Yield (Selectivity)$^{b)}$/% 10	11
COOEt COOEt	 COOMe	100	28 (28)	72 (72)
CN CN		100	0 (0)	100 (100)
COOEt COOEt	 COOMe	28	28 (100)	0
CN CN		10	10 (100)	0
COOEt COOEt	 COOMe	18	18 (100)	0
CN CN		27	27 (100)	0

a) Reaction conditions: **8**: 1.0 mmol; **9**: 2.0 mmol, catalyst: 30 wt% Cs_2CO_3/Al_2O_3 (calcined at 450 °C for 6 h) 100 mg; solvent: toluene 4 mL; temperature: 80 °C; period: 6 h. b) Selectivities for **10** and **11** are shown in parentheses.

Active Species for the Catalysis. Figure 6a shows the FT-IR spectra of Cs_2CO_3 and CsOAc supported on Al_2O_3. 30 wt% Cs_2CO_3/Al_2O_3 has typical absorbance of CO_3^{2-} at 1540 cm^{-1} for both dried and calcined samples, which are assigned to carbonate.[40] 30 wt% $CsOAc/Al_2O_3$ has the absorbance of OAc^- at 1580 cm^{-1} assigned to an acetyl group.[41] However, the absorbance at 1540 cm^{-1} appeared after the calcination at 450 °C. This suggests two possibilities for the formation of Cs_2CO_3: one is the formation of Cs_2CO_3 by the absorption of CO_2 in air, and the other is the formation of Cs_2CO_3 from CsOA by the calcination at 450 °C. Laspéras and his co-workers suggest that faujasite zeolites, CsNaX and CsNaY prepared by the impregnation of CsOAc were decomposed to Cs_2O species by calcination at 550 °C under 80% N_2 and 20% O_2 atmosphere.[42] Thus, Cs_2O species were formed from CsOAc in the absence of CO_2. These results suggest that Cs_2CO_3 species come from atmospheric CO_2. However, further studies are necessary to understand how Cs_2CO_3 species are derived from CsOAc.

FT-IR spectra of $CsNO_3$ supported on Al_2O_3 are shown Figure 6b. 30 wt% $CsNO_3/Al_2O_3$ has characteristic absorbances at 2420, 1760, and 1680 cm^{-1} assigned to NO_3^- species,[43] even after the calcination at 450 °C, however the absorbances due to NO_3^- species disappeared after the calcination at 700 °C. Consequently, broad absorbance at 1540 cm^{-1} appeared after the calcination of 30 wt% $CsNO_3/Al_2O_3$. This absorbance can be assigned to CO_3^-. These results indicate that $CsNO_3$ is stable at 450 °C, and decomposed at 700 °C.[44] The formation of Cs_2CO_3 was not extensive by the calcination at 700 °C judging from the lower activity for the Michael addition. This is probably due to deficiency of carbonate source in air at 700 °C, and the Cs species are thought to be cesium aluminate by combining with Al_2O_3 although clear XRD patterns did not appear.[45,46] Thus, the change of Cs species influences to the activities for the Michael addition. The moderate activity by the calcination at 700 °C is due to Cs_2CO_3, and cesium aluminate is not active for the reaction.

XRD patterns of the cesium catalysts are shown in Figure 7. 30 wt% Cs_2CO_3/Al_2O_3 and 30 wt% $CsOAc/Al_2O_3$ had no distinct diffractions by the loading and calcination. 30 wt% $CsNO_3/Al_2O_3$ had very sharp and strong diffractions assigned to $CsNO_3$, however these diffractions disappeared completely after the calcination at 700 °C. These results correspond to IR results discussed above.

We can discuss the active species based on the results in this paper. The most probable active species for the catalysis are Cs_2CO_3 supported on Al_2O_3. CsOAc, itself, has only low selectivity for the Michael addition, however the catalytic activities appeared after the calcination at 450 °C, where CsOAc converted to Cs_2CO_3. $CsNO_3/Al_2O_3$ kept $CsNO_3$ after the calcination at 450 °C. No significant catalytic activity was

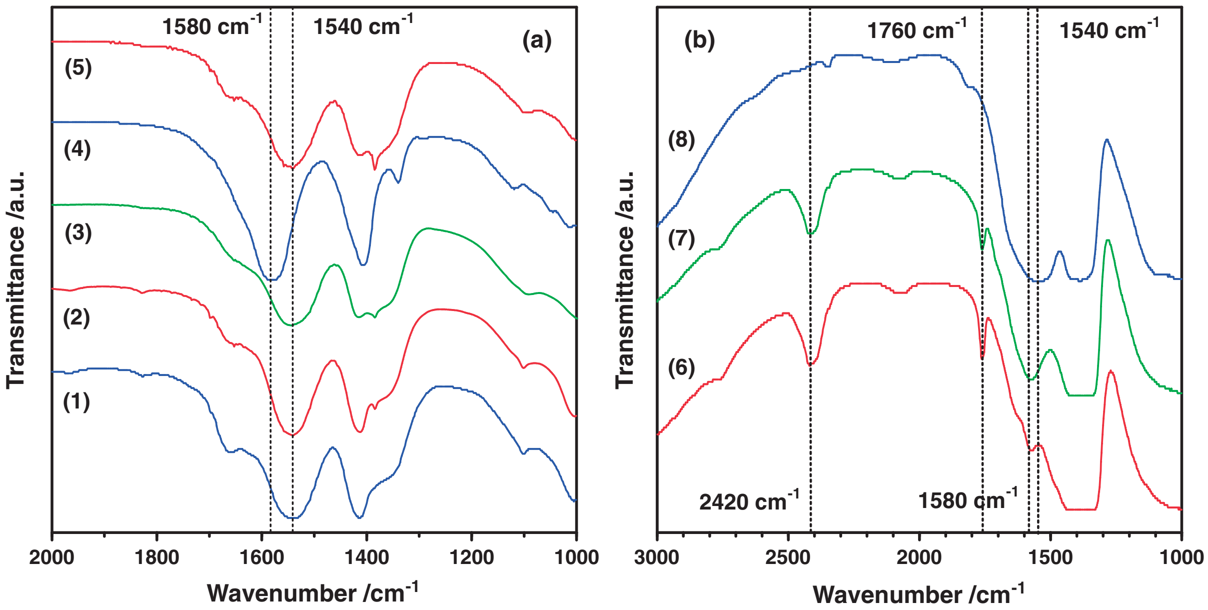


Figure 6. Effects of cesium precursor of 30 wt% Cs/Al_2O_3 on FT-IR spectra. (a) 30 wt% Cs_2CO_3/Al_2O_3 and 30 wt% CsOAc/Al_2O_3 and (b) 30 wt% $CsNO_3/Al_2O_3$. 1: Cs_2CO_3 dried at 40 °C; 2: Cs_2CO_3 calcined at 450 °C; 3: Cs_2CO_3 calcined at 700 °C; 4: CsOAc dried at 40 °C; 5: CsOAc calcined at 450 °C. 6: $CsNO_3$ dried at 80 °C; 7: $CsNO_3$ dried at 450 °C; 8: $CsNO_3$ calcined at 700 °C.

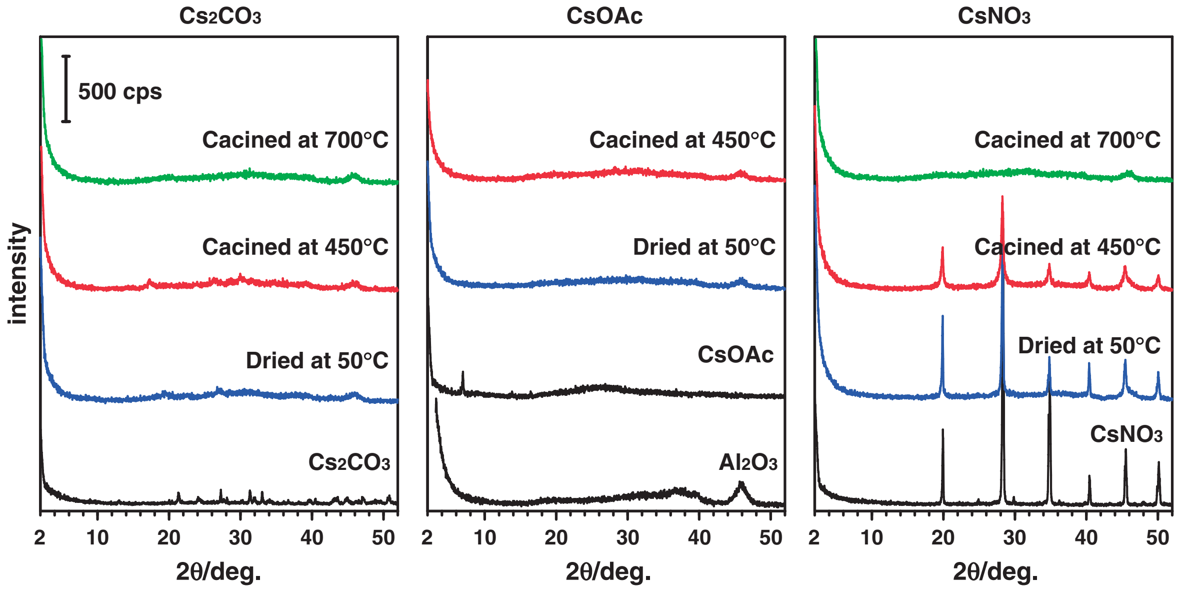


Figure 7. Effects of cesium precursor of 30 wt% Cs/Al_2O_3 on XRD patterns.

observed by $CsNO_3/Al_2O_3$ dried at 40 °C and calcined at 470 °C, because the salt has no base characteristics. The catalytic activities appearing on Cs/Al_2O_3 after the calcination at 700 °C are probably due to the formation of Cs_2CO_3, and the lower activity should be due to the formation of cesium aluminate species on the surface. Yamaguchi and his co-workers proposed a new cesium active species appeared by the calcination of cesium salt under evacuation at 750 °C.[12,13] The differences from our results should be due to the atmosphere of the calcination.

Cs_2CO_3, itself, showed high activity corresponding to 30 wt% Cs_2CO_3/Al_2O_3. Higher dispersed Cs_2CO_3 on Al_2O_3 as shown in Tables 3 and 4 have lower catalytic activity for the Michael addition even by use of the same cesium amount. These results indicate that moderately dispersed to bulk Cs_2CO_3 is appropriate for the high performance of the catalysis.

The Cs_2CO_3 species works as an efficient base catalyst for the Michael additions, which occur by typical base catalysis mechanism.[3] The reaction is started by proton extraction from an active methylene of donor such as **1** by Cs_2CO_3, following attack of the anion complex to the double bond of the methyl acrylate, resulting in the formation of the anion complex of adduct. The catalysis gives the product by protonation of the resultant anion complex. The results in this work indicate that Cs_2CO_3 is sufficiently basic for the catalysis of the Michael addition.

Advantages of Cs_2CO_3 Supported on Alumina in the Base Catalysis. Although Cs_2CO_3 is a well-known versatile base catalyst in organic synthesis,[25–37] it is tedious to separate the organic products from the catalyst. However, Cs_2CO_3/Al_2O_3 after the reaction in toluene as solvent can be separated from the organic products by simple filtration. Moreover, catalytic activity of Cs_2CO_3/Al_2O_3 was easily recovered after the calcination of the catalysts used for the reactions.

These results suggest that the use of Cs_2CO_3/Al_2O_3 could be a green catalyst to reduce the environmental burden of chemical processes.

Conclusion

The cesium salts supported on γ-Al_2O_3 were highly active catalysts for the Michael addition of diethyl malonate (**1**) to methyl acrylate (**2**) in toluene as the solvent. Principal product was diethyl [2-(methoxycarbonyl)ethyl]malonate (**3**), and the formation of diethyl bis[2-(methoxycarbonyl)ethyl]malonate (**4**) was enhanced by the increase in the amounts of **2**. The use of malononitrile was enhanced the formation of diadduct as principal products in the reaction with methyl acrylate. Other methyl acrylates, such as methyl methacrylate and methyl crotonate, gave low yield of the products. Active species for the catalysis are thought to be Cs_2CO_3 on the catalysts formed from Cs_2CO_3, CsOAc, and $CsNO_3$.

The catalysts after the reaction in toluene can be separated from the organic products by simple filtration. The catalysts were easily recycled and the catalytic activity of Cs_2CO_3/Al_2O_3 was recovered by the calcination of recycled catalysts. Cs_2CO_3/Al_2O_3 is expected to be a versatile green catalyst for many organic reactions, including the Michael, Knoevenagel, and aldol reactions. We will describe further applications of Cs_2CO_3/Al_2O_3 in the near future.

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Supporting Information

Figure S1: XRD patterns of Cs_2CO_3 loaded MCM-41. Figure S2: N_2 adsorption isotherm of Cs_2CO_3 loaded MCM-41. These materials are available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

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