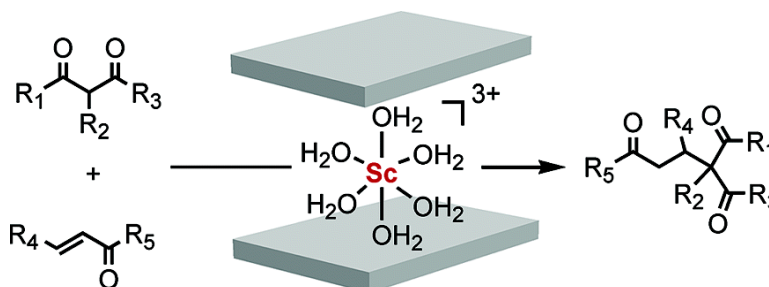


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A Novel Montmorillonite-Enwrapped Scandium as a Heterogeneous Catalyst for Michael Reaction

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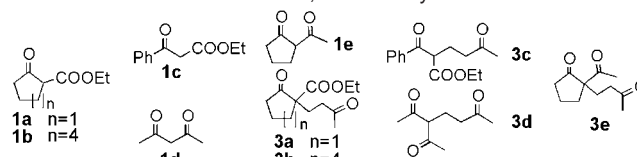
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The Michael reaction of 1,3-dicarbonyl compounds with enones has provided a powerful method for the synthesis of 1,5-dioxo units as valuable intermediates in steroid chemistry.¹ In a quest for improving the reaction, various metal complexes have been developed as Lewis acid catalysts instead of conventional strong bases.² From the environmental standpoint, the reaction in water as the solvent is desirable and has been reported with the use of rare earth metal complexes.³ Among these, rare earth metal trifluoromethanesulfonates [RE(OTf)₃] are known as water-compatible catalysts,⁴ in which the RE³⁺ aqua complexes, surrounded by the less-nucleophilic OTf counteranions in the second coordination sphere, can act as Lewis acids.⁵ In particular, Sc(OTf)₃ is promising because of its significantly stronger acidity in comparison with that of other RE(OTf)₃.⁶

Montmorillonites, hereafter referred to as monts, are hydrophilic clays and can be structurally defined as layers of negatively charged two-dimensional silicate sheets that are separated by interlayer cationic species with high exchange ability for other metal polycations.⁷ Recently, we found that various metal cations are successfully introduced within the interlayers, via a simple ion-exchange method, to afford metal ion species in unique structures as efficient solid catalysts.⁸ In this contribution, we describe an Sc³⁺ aqua complex that is enwrapped within the interlayer spaces of monts, using the silicate sheet as the macrocounteranion having low nucleophilicity.⁹ This Sc³⁺-exchanged mont (Sc³⁺-mont) was demonstrated to function as an efficient catalyst for the Michael reaction of 1,3-dicarbonyls in heterogeneous systems.¹⁰ Our protocol can be considered as environmentally friendly due to the following reasons: (1) employment of a nearly stoichiometric amount of the acceptors,³ (2) use of water as the solvent, and (3) ability to recycle the solid catalyst.

Numerous metal cation-exchanged monts (Mⁿ⁺-monts) were prepared by treatment of Na⁺-mont (Kunipia F, Kunimine Industry Co. Ltd.; Na, 2.69; Al, 11.8; Fe, 1.46; Mg, 1.97%) with aqueous solution of various metal triflates. For example, a Sc³⁺-mont was obtained from Sc(OTf)₃ (Sc content: 0.396 mmol g⁻¹) as a light-gray powder.^{11,12} X-ray diffraction studies verified the retention of its layered structure with a basal spacing of 3.6 Å, and its XPS spectra (Sc 2p_{3/2} = 402.6 eV) revealed the formation of trivalent Sc species. The lack of peaks in the vicinity of 2.8 Å in the Fourier transform of k³-weighted Sc K-edge EXAFS showed that the Sc species is monomeric. The peak at 1.7 Å was assignable to an Sc–O moiety; the interatomic distance and the coordination number were 2.13 Å and 6, respectively.¹³ Conclusively, a monomeric aqua Sc ion **I** is formed within the interlayer of the mont. It has been reported that, under aqueous conditions, a homogeneous aqua complex, [Sc(H₂O)₆]³⁺, readily underwent hydrolysis to yield OH-bridged dimers and trimers.¹⁴ The present preparation method, which involves the cation-exchange ability of monts, can provide a powerful protocol

Table 1. Michael Reaction of 1,3-Dicarbonyls with **2a** in Water^a



entry	catalyst	donor	product	temp. (°C)	time (h)	yield ^b (%)
1	Sc ³⁺ -mont	1a	3a	30	0.5	99
2	Sc(OTf) ₃	1a	3a	30	0.5	7
3	Y ³⁺ -mont	1a	3a	30	0.5	83
4	Yb ³⁺ -mont	1a	3a	30	0.5	62
5	La ³⁺ -mont	1a	3a	30	0.5	62
6	Zn ²⁺ -mont	1a	3a	30	0.5	3
7	no	1a	3a	30	0.5	0
8 ^c	Sc ³⁺ -mont	1b	3b	60	2	80
9	Sc ³⁺ -mont	1c	3c	50	2	97
10	Sc ³⁺ -mont	1d	3d	45	3	98
11	Sc ³⁺ -mont	1e	3e	50	1	97

^a Reaction conditions; active metal species (0.04 mmol), donor (2 mmol), **2a** (2.2 mmol), H₂O (3 mL). The order of the Lewis acidity of Mⁿ⁺ triflates is as follows: Sc (1.00) ≫ Y (0.85) > Yb (0.83) > La (0.82) ≫ Zn (0.71). The values of parentheses were the binding energy of Mⁿ⁺ with O₂^{•-}. See ref 16 in detail. ^b Yields of products were determined by GC based on donor. ^c Sc³⁺-mont (0.05 g), **1b** (0.5 mmol), **2a** (0.55 mmol), water (1 mL).

for the stabilization of monomeric metal species within the interlayers of monts to serve as a heterogeneous catalyst.

Initially, Michael reactions of ethyl 2-oxocyclopentanecarboxylate **1a** with 3-buten-2-one **2a** (1.1 equiv) in the presence of Mⁿ⁺-mont catalysts were carried out using various solvents,¹¹ in which water was the optimal solvent with respect to the yield of ethyl 2-oxo-1-(3-oxobutyl)cyclopentanecarboxylate **3a**.¹⁵

As shown in Table 1, higher yields of **3a** were obtained with increasing Lewis acidity of the metal cations (entries 1, 3–6),¹⁶ and accordingly, the most acidic Sc³⁺-mont corresponded to the highest yield of **3a** (entry 1). This trend clearly demonstrates that the Lewis acid sites of the Mⁿ⁺-monts play an important role in the above Michael reactions. Furthermore, the Sc³⁺-mont exhibited significantly higher catalytic activities than the homogeneous Sc(OTf)₃ complex (entry 2). Since elemental analysis showed the absence of the OTf groups in the solid catalyst, the remarkable catalytic activity of Sc³⁺-mont might be attributable to the low nucleophilic silicate layers as the macroanions.⁹ Under aqueous conditions, the Michael reactions were extended to other 1,3-dicarbonyl substrates (entries 8–11).

Treatment of a 1:1 mixture of **1a** and **1b** with acceptor **2a** in the presence of the Sc³⁺-mont catalyst in water afforded **3a** predominantly.¹⁷ This preference can be attributed to highly hydrophilic character of the Sc³⁺-mont, in which water molecules on the interlamellar surfaces exclude the more hydrophobic **1b** from a

Table 2. Michael Reaction by Sc³⁺-mont without Solvents^a

entry	donor	acceptor	product	temp. (°C)	time (h)	yield ^b (%)
1	1a	2a	3a	20	3	97
2 ^c	1b	2a	3b	50	4	80
3	1c	2a	3c	50	1	99
4	1d	2a	3d	40	2	94
5	1e	2a	3e	50	1	99
6	1a	2b	3f	40	2	96
7	1a	2c	3g	70	5	99 ^d
8	1a	2d	3h	70	4	98 ^d
9 ^e	1a	2e	3i	160	2	70
10 ^e	1f	2c	3j	120	2	91

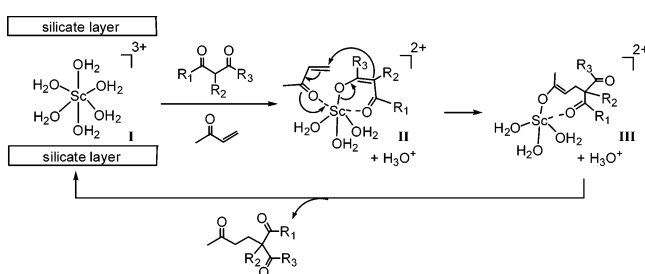
^a Reaction conditions; Sc³⁺-mont (0.1 g, Sc: 0.04 mmol), donor (4 mmol), acceptor (4.4 mmol). ^b Yields of products were determined by GC based on donor. ^c Sc³⁺-mont (0.025 g), **1b** (1 mmol), **2a** (1.5 mmol). ^d A 1:1 diastereomeric mixture. ^e A stainless steel autoclave was used; Sc³⁺-mont (0.1 g), donor (1 mmol), acceptor (1.1 mmol), CH₃CN (1 mL).

catalytic site of Sc³⁺ species. This selectivity is markedly in contrast to that of the Brønsted acid–surfactant-combined catalyst.¹⁸

Upon completion of the reaction, the Sc³⁺-mont catalyst was readily separated from the reaction mixture by simple filtration and could be reused without any appreciable losses of its high activity and selectivity. For the reaction of **1a** with **2a**, over 98% yields for **3a** were obtained during the three recycling experiments.¹¹ In comparison to the fresh catalyst, the spent one retained its Sc content, and furthermore, maintained its original monomeric Sc³⁺-structure, as determined by XAFS. To confirm whether the Michael reaction occurs at the monomeric Sc species on the mont solid, the Sc³⁺-mont, in the case of the reaction of **1a** with **2a**, was removed by filtration after ca. 50% conversion of **1a** at the reaction temperature. Further treatment of the filtrate under similar reaction conditions did not afford any product **3a**.

It is notable that the Sc³⁺-mont can efficiently catalyze the Michael reaction under solvent-free conditions, as summarized in Table 2. 3-Buten-2-one **2a** readily reacted with a variety of β-keto esters and 1,3-diketones to afford the corresponding 1,5-dioxo compounds in high yields (entries 1–5). Furthermore, 1-penten-3-one **2b**, 2-cyclopenten-1-one **2c**, and 2-cyclohexene-1-one **2d** were also found to be good acceptors (entries 6–8). Less reactive substrates such as diethyl malonate **1f** and ethyl acrylate **2e** required higher reaction temperatures (entries 9 and 10). In all cases, 1,4-addition products were exclusively obtained. A 100-mmol scale reaction of **1a** with **2a** was successfully carried out without any solvents to afford **3a** in 91% yield after 2 h; the number of turnovers (TON) of the Michael adduct based on Sc exceeded 1000. To the best of our knowledge, among the Lewis acid catalysts reported to date, *this Sc³⁺-mont has shown the highest catalytic activity, in terms of TON, for the Michael reaction of 1,3-dicarbonyls with enones.*^{2,3}

As illustrated in Scheme 1, the Michael reaction possibly proceeds via formation of a scandium complex **II**, in which both the 1,3-dicarbonyl compound and the enone coordinate to the Sc center. Subsequently, the successive carbon–carbon bond formation produces an intermediate Sc-alcoholate **III**, followed by protolysis to afford the Michael adduct together with the regeneration of the original Sc species **I**. Importance of the coordination of both reactants is evident from the following separate experiments: (i) treatment of **I** with **1d** gave an acetylacetonato Sc species in the

Scheme 1

Sc³⁺-mont,¹⁹ and (ii) Sc(acac)₃ did not catalyze the Michael reaction of **1d** with **2a**.²⁰

In conclusion, the monomeric Sc species, having hexacoordinated aqua ligands, was formed within the interlayers of montmorillonite via a remarkably simple method. This protocol provided a highly active heterogeneous catalyst for Michael reactions under aqueous or solvent-free conditions. Moreover, this catalyst was reusable without any appreciable losses in its high activity and selectivity. Further application to asymmetric catalysis remains to be exploited.

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Supporting Information Available: Experimental details and curve fitting analysis (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- Jung, M. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 4, pp 1–67.
- For an excellent review on transition metal-catalyzed Michael reaction of 1,3-dicarbonyls, see: Christoffers, J. *Eur. J. Org. Chem.* **1998**, 1259.
- For examples of the Michael reaction in water, see: (a) Keller, E.; Feringa, B. L. *Tetrahedron Lett.* **1996**, 37, 1879. (b) Kotsuki, H.; Arimura, K. *Tetrahedron Lett.* **1997**, 38, 7583. (c) Mori, Y.; Kakumoto, K.; Manabe, K.; Kobayashi, S. *Tetrahedron Lett.* **2000**, 41, 3107. Note that the above systems generally require 1.5–3 equiv of the acceptors to achieve high yields within acceptable reaction times.
- For a review, see: Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, 102, 2227.
- Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, 35, 209.
- For a review, see: Kobayashi, S. *Eur. J. Org. Chem.* **1999**, 15.
- (a) Pinnavaia, T. J. *Science* **1983**, 220, 365. (b) Laszlo, P. *Science* **1987**, 235, 1473.
- (a) Ebitani, K.; Kawabata, T.; Nagashima, K.; Mizugaki, T.; Kaneda, K. *Green Chem.* **2000**, 2, 157. (b) Kawabata, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *Tetrahedron Lett.* **2001**, 42, 8329. (c) Ebitani, K.; Ide, M.; Mitsudome, T.; Mizugaki, T.; Kaneda, K. *Chem. Commun.* **2002**, 690.
- Onaka, M. *Yuki Gosei Kagaku Kyokaiishi* **1995**, 53, 392.
- For recent reports on heterogeneous Michael reactions using organic polymer-bound Sc catalysts, see: (a) Nagayama, S.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2000**, 39, 567. (b) Reetz, M. T.; Giebel, D. *Angew. Chem., Int. Ed.* **2000**, 39, 2498. (c) Weiqiang, G.; Zhou, W.-J.; Gin, D. L. *Chem. Mater.* **2001**, 13, 1949. Note that these systems are limited to the reaction of activated donors such as silyl enol ethers.
- See Supporting Information for details.
- Elemental analysis (Sc, 1.78; Na, 0.04%) supported that one Sc³⁺ ion completely substituted three equivalents of Na⁺ ions.
- The distance between scandium and oxygen atoms in the Sc³⁺-mont is comparable to that observed in hexa-coordinated scandium aqua complexes (2.11–2.12 Å); see: Cotton, S. A. *Polyhedron* **1999**, 18, 1691.
- Brown, P. L.; Ellis, J.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1983**, 35.
- When soaked in water, the interlayer distance of the Sc³⁺-mont expanded from 3.6 to 9.0 Å, as determined by XRD, allowing access of the substrates to the catalytic site of Sc species.
- Fukuzumi, S.; Ohkubo, K. *J. Am. Chem. Soc.* **2002**, 124, 10270.
- Treatment of **1a** and **1c** with **2a** under solvent-free conditions afforded **3a** and **3c** in 91% and 54% yields, respectively.
- Manabe, K.; Iimura, S.; Sun, X.-M.; Kobayashi, S. *J. Am. Chem. Soc.* **2002**, 124, 11971.
- The IR absorption bands at 1578 and 1530 cm⁻¹ confirmed the formation of an acetylacetonato Sc complex; see: Singh, P. R.; Sahai, R. *Inorg. Chim. Acta* **1968**, 2, 102.
- For Fe(acac)₃, the activation of an acceptor by the Lewis acid sites is indispensable; see: Christoffers, J. *Chem. Commun.* **1997**, 943.

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