

Monomeric Metal Aqua Complexes in the Interlayer Space of Montmorillonites as Strong Lewis Acid Catalysts for Heterogeneous Carbon–Carbon Bond-Forming Reactions

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Abstract: Montmorillonite-enwrapped copper and scandium catalysts (Cu^{2+} - and Sc^{3+} -monts) were easily prepared by treating Na^+ -mont with the aqueous solution of the copper nitrate and scandium triflate, respectively. The resulting Cu^{2+} - and Sc^{3+} -monts showed outstanding catalytic activities for a variety of carbon–carbon bond-forming reactions, such as the Michael reaction,

the Sakurai–Hosomi allylation, and the Diels–Alder reaction, under solvent-free or aqueous conditions. The remarkable activity of the mont catalysts is attributable to the negatively charged

silicate layers that are capable of stabilizing metal cations. Furthermore, these catalysts were reusable without any appreciable loss in activity and selectivity. The Cu^{2+} -mont-catalyzed Michael reaction proceeds via a ternary complex in which both the 1,3-dicarbonyl compound and the enone are coordinated to a Lewis acid Cu^{2+} center.

Keywords: C–C bond formation • heterogeneous catalysis • Lewis acids • montmorillonite

Introduction

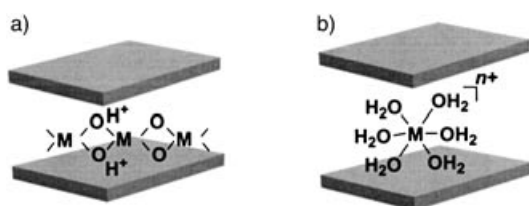
Lewis acids are of great interest because of their ability to catalyze a wide variety of carbon–carbon bond-forming reactions.^[1] They can replace traditional Brønsted acids and bases to achieve green organic transformations.^[2] Many manufacturing reactions for fine chemicals and pharmaceuticals rely on homogeneous Lewis acid catalysts. However, these reactions often require the tedious isolation of products or the removal of large volumes of salt wastes during neutralization of homogeneous acids.^[1] To overcome these disadvantages, much effort has been devoted to the development of heterogeneous catalytic systems.^[3] In this context, numerous supported Lewis acid catalysts have been developed,^[4] however, their activities are often low because strong interactions between the Lewis acid centers and their supports result in decreased Lewis acidities.

Another promising synthetic approach to environmentally friendly chemistry is to minimize or eliminate the use of harmful organic solvents. A paradigm shift from using solvents toward solvent-free reactions can improve outcomes and simplify organic syntheses.^[5] The use of water as a solvent is also recognized as a significant challenge in green chemistry, and additionally reveals unique catalytic activities not observed under dry conditions.^[6]

Montmorillonites, referred to as monts, are hydrophilic clays with a layered structure. They are of considerable interest as environmentally benign and reusable catalysts. Owing to their ion-exchange properties, various types of metal cations can be introduced readily into their expansible interlayer spaces.^[7,8] In the course of our studies on the metal-cation-exchanged montmorillonite catalysts (M^{n+} -mont), we have defined two types of metal ion species with unique structures within the interlayers of the mont: chain-like metal species for Ti and Fe (Scheme 1a), and a monomeric aqua complex for Sc (Scheme 1b). These M^{n+} -monts exhibited excellent catalytic performance in various organic transformations.^[9]

We present novel montmorillonite-enwrapped monomeric complexes of Cu and Sc, which can be prepared readily and can act as highly active Lewis acid catalysts for a variety of important carbon–carbon bond-forming reactions, such as the Michael reaction, the Sakurai–Hosomi allylation, and

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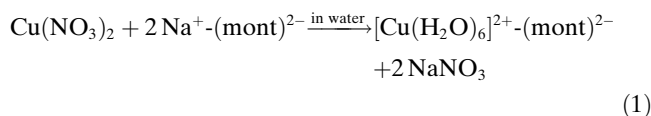
Scheme 1. Schematic structures of the M^{n+} -monts: (a) a chain-like metal species and (b) a monomeric aqua complex.

the Diels–Alder reaction, under solvent-free or aqueous conditions. These heterogeneous reaction systems have the advantages of eliminating waste production and simplifying the workup procedure. Furthermore, the mont catalysts are reusable without an appreciable loss of activity and selectivity. We believe the application of catalytic systems based on monts as a macroanion goes beyond mere immobilization and will lead to the development of high-performance heterogeneous Lewis acid catalysts for ‘green’ organic syntheses.

Results and Discussion

Preparation and characterization of montmorillonite-enwrapped metal cations: The mont-enwrapped metal cation species, Cu, Sc, Y, Yb, La, and Zn, were prepared by treating Na^+ -mont with the aqueous solution of the appropriate metal nitrates or triflates. Among the products, the catalytic abilities of Cu- and Sc-monts were particularly attractive for carbon–carbon bond-forming reactions.

Cu-mont: The Cu-mont was prepared by treatment of Na^+ -mont with aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ [Eq. (1)]. On the basis of the X-ray diffraction (XRD) analysis, the layered structure was identified and the basal spacing for the Cu-mont was estimated to be $2.9 \text{ \AA}$, which is comparable to that of the parent Na^+ -mont. Elemental analysis confirmed that two Na^+ ions are replaced by one Cu^{2+} ion during ion-exchange (Cu 3.21; Na 0.09%).



UV/Vis spectra of the Cu-mont exhibited an absorption peak at 1.7 eV , which is similar to that of Cu^{2+} -exchanged zeolites with Cu^{II}O_6 octahedral species within their pores.^[10,11] Figure 1 shows Cu K-edge X-ray absorption near-edge structure (XANES) spectra of the Cu-mont and Cu reference compounds. The absorption edge varies with respect to the oxidation state of copper, and the XANES spectrum of Cu_2O has a strong peak due to the $1s-4p\pi^*$ transition near 8980 eV .^[12] The XANES spectrum of the Cu-mont resembles that of the CuO with a distorted octahedral coordination environment,^[13] but differs from those of Cu foil

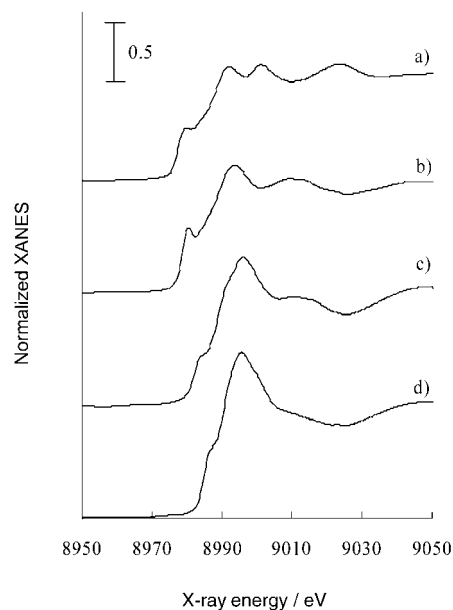


Figure 1. Normalized Cu K-edge XANES spectra of (a) Cu foil, (b) Cu_2O , (c) CuO , and (d) Cu^{2+} -mont.

and Cu_2O in shape and position of the edge, supporting formation of a divalent Cu ion. Figure 2a depicts the Fourier transform (FT) of the k^3 -weighted Cu K-edge extended X-ray absorption fine structure (EXAFS) of the Cu^{2+} -mont.

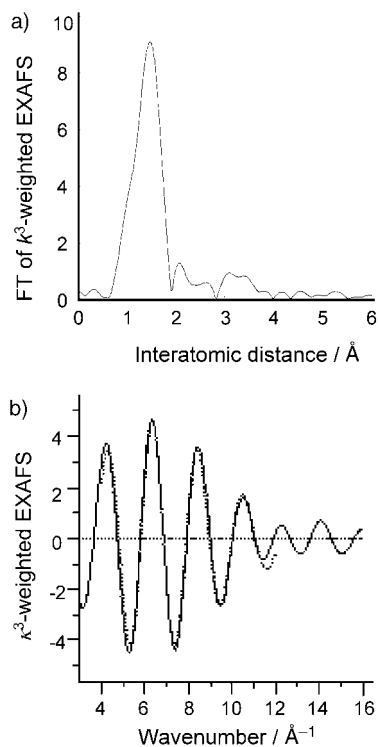


Figure 2. (a) FT magnitude of k^3 -weighted EXAFS of the Cu^{2+} -mont, and (b) inverse FT of the peaks with the $1.1 < R \text{ \AA}^{-1} < 1.9$ range in (a). Phase shift was not corrected in (a). The dotted line in (b) showed the result of a curve-fitting analysis using two Cu–O shell parameter in the range $4\text{--}12 \text{ \AA}^{-1}$.

The peak at 1.5 Å was assignable to a Cu–O moiety (Figure 2b).^[14]

The results of the curve-fitting analysis (Table 1) show a slightly distorted CuO₆ octahedron with four short (1.90 Å) and two long (2.03 Å) Cu–O shells. Because of the restrict-

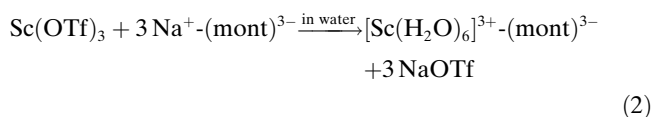
Table 1. Results of curve-fitting analysis of the Cu–O and Sc–O shells for mont-enwrapped Cu²⁺ and Sc³⁺ catalysts

Sample	Shell	CN ^[a]	R ^[b] [Å]	Δσ ^[c] [Å ²]
Cu ²⁺ -mont				
	fresh			
	Cu–O (1)	4.0	1.90	0.0005
	Cu–O (2)	2.0	2.03	0.0004
	recovered ^[d]			
	Cu–O (1)	4.0	1.92	0.0025
in substrates ^[e]	Cu–O (2)	2.0	2.03	0.0028
	Cu–O (1)	2.1	1.93	0.0006
	Cu–O (2)	1.0	2.39	0.0065
	Cu–O (3)	2.1	1.86	0.0009
	Cu–O (4)	1.0	2.60	0.0063
Sc ³⁺ -mont				
	fresh			
fresh	Sc–O	6.0	2.13	0.0019
recovered ^[f]	Sc–O	6.1	2.13	0.0014

[a] Coordination number. [b] Interatomic distance. [c] Δσ is the difference between the Debye–Waller factor of the sample and that of the reference material. [d] The recovered catalyst by filtration after the Michael reaction of ethyl 2-oxocyclopentanecarboxylate (**1a**) with 2-cyclohexen-1-one (**2a**) under solvent-free conditions (see text). [e] The catalyst treated with both **2a** and acetylacetone (**1c**). [f] The recovered catalyst after the Michael reaction of **1a** with 3-buten-2-one (**2b**) in water (see text).

ed interlayer space of the mont, the Cu–O distance of 2.03 Å is shorter than the axial Cu–O bond of 2.43 Å observed in a [Cu(H₂O)₆]²⁺ complex in perchlorate solution.^[15] In the FT EXAFS, the peaks above 2 Å, attributed to the presence of contiguous Cu sites, were not detectable for the Cu²⁺-mont. Based on the basal spacing and the Cu–O distances of the Cu²⁺-mont, it is reasonable to assume that the monomeric Cu aqua complex in the interlayer is inclined at about 45° with respect to the *c* axis of the mont. An analogous [Cu(H₂O)₆]²⁺ species has been reported within the interlayer space of hecrites^[7b,16] and the pores of zeolite-X.^[10]

Sc-mont: Treatment of Na⁺-mont with aqueous Sc(OTf)₃ afforded Sc-mont [Eq. (2)]. Elemental analysis (Sc 1.78, Na 0.04%) of the Sc-mont showed that three Na⁺ ions are replaced by one Sc ion.



XRD studies verified that the layered structure of the Sc-mont is retained with a basal spacing of 3.6 Å. X-ray photoelectron spectroscopy (XPS) revealed formation of a trivalent Sc species. Fourier transform of *k*³-weighted Sc K-edge EXAFS of the Sc₂O₃ had a broad peak near 3.0 Å due to Sc–Sc and Sc–O shells in the second coordination sphere (Figure 3). In contrast, the lack of this peak for the Sc³⁺-mont samples supported the presence of a monomeric Sc

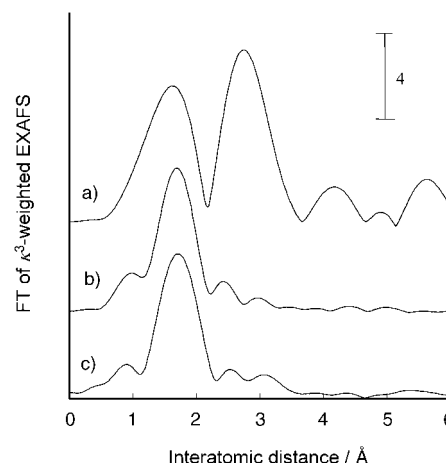


Figure 3. Fourier transforms of *k*³-weighted Sc K-edge EXAFS of (a) Sc₂O₃, (b) fresh Sc³⁺-mont, and (c) recovered Sc³⁺-mont after the Michael reaction of **1a** with **2b** (see text). Phase shift was not corrected.

species. The peak at 1.7 Å was assignable to a Sc–O shell and curve-fitting results revealed that the interatomic distance (*R*) and the coordination number (CN) of the Sc–O bond were 2.13 Å and 6.0, respectively (Table 1).

A monomeric aqua Sc ion is clearly formed within the interlayer of the mont. The distances between the scandium and oxygen atoms in the Sc³⁺-mont are comparable to those observed in hexacoordinate scandium aqua complexes, such as [Sc(H₂O)₄(picrate)₂]⁺ (2.109 Å),^[17] [Sc(H₂O)₄(tosylate)₂]⁺ (2.117 Å),^[18] and [ScCl₃(H₂O)₃] [H₂L]·3H₂O (2.122 Å).^[19]

The situations involving Cu²⁺ and Sc³⁺ ions contrast sharply with that of the Ti⁴⁺ ion in the mont interlayer, where the Ti cations form a chainlike structure linked by Ti–O–Ti moieties.^[9a–d] We think that this difference can be explained by the hydrolysis constant (*K_h*) of the metal cations.^[20] Metal cations with small *pK_h* values (2.3 for Ti⁴⁺) generally are easy to hydrolyze to the corresponding [M(OH)_{*n*}]⁺ cation species that are precursors to the M–O–M moiety. However, Cu and Sc cations have large *pK_h* values (7.53 for Cu²⁺ and 4.3 for Sc³⁺), and thus are stable against hydrolysis and remain monomeric.

The present preparation method, which utilizes the cation-exchange ability of monts, is a powerful protocol for the stabilization of monomeric aqua metal species of Cu and Sc within the interlayer of monts for use as heterogeneous acid catalysts.

Michael reaction using the Cu²⁺-mont catalyst: The Michael reaction of 1,3-dicarbonyl compounds with enones provides access to 1,5-dioxo synthons, which can be transformed easily into cyclohexenone derivatives for use as important intermediates in steroid and terpenoid synthesis.^[21] The Michael reactions of ethyl 2-oxocyclopentanecarboxylate (**1a**) with 2-cyclohexen-1-one (**2a**) in various solvents were conducted in the presence of the Cu²⁺-mont (Table 2). Nitromethane was an optimal solvent to give 2-oxo-1-(3-oxocyclohexyl)-cyclopentanecarboxylate (**3a**) in 82% yield (Table 2,

Table 2. Michael reaction of **1a** with **2a** using various M^{n+} -mont catalysts.^[a]

Entry	Catalyst	Solvent	Yield [%] ^[b,c]
1	Cu^{2+} -mont	neat	96
2	Cu^{2+} -mont	nitromethane	82
3	Cu^{2+} -mont	EtOH	76
4	Cu^{2+} -mont	<i>n</i> -hexane	69
5	Cu^{2+} -mont	toluene	46
6	Cu^{2+} -mont	ethyl acetate	43
7	Cu^{2+} -mont	1,2-dichloroethane	32
8	Cu^{2+} -mont	acetonitrile	6
9	Cu^{2+} -mont	water	6
10	Cu^{2+} -mont	DMA	0
11	Cu^{2+} -mont	DMF	0
12	Cu^{2+} -mont	DMSO	0
13	Sc^{3+} -mont	neat	63
14	Y^{3+} -mont	neat	25
15	Yb^{3+} -mont	neat	20
16	La^{3+} -mont	neat	16
17	Zn^{2+} -mont	neat	11
18	Na^{+} -mont	neat	trace
19	$Cu(NO_3)_2 \cdot 3H_2O$	neat	59
20	no	neat	0

[a] Reaction conditions; active metal species (0.05 mmol), **1a** (4 mmol), **2a** (6 mmol), solvent (5 mL) (entries 2–12), 70 °C, 2 h. [b] Yields of products were determined by GC based on donor. [c] A 1:1 ratio of diastereoisomers.

entry 2). Ethanol and *n*-hexane were also effective solvents, affording 76 and 69 % yields of **3a**, respectively (Table 2, entries 3 and 4). In marked contrast to the Sc^{3+} -mont-catalyzed Michael reaction,^[9f] vide infra, water was a poor solvent (Table 2, entry 9). Interestingly, the Cu^{2+} -mont exhibited the greatest catalytic activity under neat conditions (Table 2, entry 1).^[22]

The catalytic activity for the Michael reaction without solvents was compared by using various M^{n+} -monts. The Cu^{2+} -mont gave the highest yield of **3a** (Table 2, entry 1 versus entries 13–17). The Michael reaction did not occur in the presence of the parent Na^{+} -mont (Table 2, entry 18). Notably, catalytic activity of the Cu^{2+} -mont was greater than that of a homogeneous $Cu(NO_3)_2 \cdot 3H_2O$ (Table 2, entry 19). The yield of **3a** increased with an increase in Lewis acid strength of the metal cation in the mont.^[23]

The scope of substrates for the Michael reaction catalyzed by the Cu^{2+} -mont under solvent-free conditions was examined (Table 3). The Michael reactions of various β -keto esters and 1,3-diketones with 3-buten-2-one (**2b**) occurred efficiently to afford the corresponding 1,5-dioxo compounds, even at room temperature (Table 3, entries 1–4). In addition, 1-penten-3-one (**2c**) also acted as a good acceptor (Table 3, entry 5). It is said that the solvent-free Michael reaction with cyclic enones using $FeCl_3 \cdot 6H_2O$ ^[24] and $Cu(OAc)_2 \cdot H_2O$ ^[25] is unsuccessful. However, the Cu^{2+} -mont was effective for such enones to give the corresponding Michael adducts within 5 h (Table 3, entries 6 and 9). In all cases, the

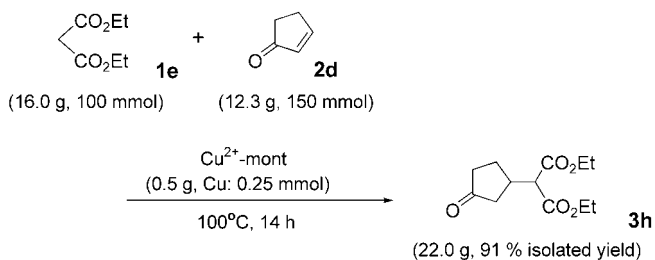
Table 3. Solvent-free Michael reaction catalyzed by Cu^{2+} -mont.^[a]

Entry	Donor	Acceptor	Product	Temp. [°C]	Time [h]	Yield [%] ^[b]
1	1a	2b	3b	20	1	99
2	1b		3c	20	1	97
3	1c		3d	20	1	97
4	1d		3e	20	1	97
5	1a	2c	3f	20	2	96
6	1a	2a	3a	70	2	92 ^[c]
7 ^[d]	1a	2a	3a	70	2	92 ^[c]
8 ^[e]	1a	2a	3a	70	2	92 ^[c]
9	1a	2d	3g	70	5	99 ^[c]

[a] Reaction conditions; Cu^{2+} -mont (Cu: 0.05 mmol), donor (4 mmol), acceptor (4.4 mmol). [b] Yields of products were determined by GC based on donor. [c] A 1:1 ratio of diastereoisomers. [d] Reuse-1. [e] Reuse-2.

desired 1,4-addition products were obtained exclusively without formation of 1,2-addition compounds.

It is noteworthy that 100 mmol of diethyl malonate (**1e**) readily reacted with 2-cyclopenten-1-one (**2d**) under solvent-free conditions with only 0.25 mol % of the Cu^{2+} -mont catalyst to afford diethyl 3-oxocyclopentylmalonate (**3h**) in a high yield (Scheme 2).

Scheme 2. Cu^{2+} -mont-catalyzed 100 mmol-scale Michael reaction under solvent-free conditions.

Generally, the Michael reaction of dialkyl malonates does not proceed easily under traditional Lewis acid catalyzed conditions,^[21d] but some base catalysts such as sodium ethoxide show high catalytic activity toward these substrates.^[21c]

Shibasaki et al. recently reported that the La-linked-BINOL catalysts were highly efficient for the asymmetric Michael reaction of dialkyl malonates with enones, in which the metal center and the naphthoxide moiety act as a Lewis acid and Brønsted base, respectively.^[26] In a similar fashion, the Michael reaction by the Cu²⁺-mont likely proceeds by bifunctional catalysis between the Lewis acid Cu complex and the silicate layer of the mont; the latter efficiently abstracts a proton from 1,3-dicarbonyl compounds.

Upon completion of the Michael reaction, the Cu²⁺-mont catalyst was readily recovered from the reaction mixture by simple filtration, and could be reused without any discernible loss in activity and selectivity. As shown in Table 3, yields of 92% were obtained in two recycling experiments (entries 7 and 8). Elemental analysis of the used Cu²⁺-mont confirmed no leaching of Cu species from the catalyst. The retention of monomeric Cu²⁺ species in the recovered Cu-mont catalyst was supported by EXAFS data (Table 1). In the reaction of **1a** with **2a**, the Cu²⁺-mont was removed by filtration after about 50% conversion of **1a** at 70°C; further treatment of the filtrate under similar reaction conditions did not afford any additional **3a**. These observations clearly demonstrate that the Michael reaction occurred at the Cu species within the mont layers.

Catalysis of the Sc³⁺-mont for Michael reactions in water:

Performing carbon–carbon bond-forming reactions in water as the solvent is of great interest because of practical and environmental considerations.^[6,27] While many Lewis acids such as Ti, Al, Sn, and B complexes are hydrolyzed to form inactive hydroxides and oxides in the presence of water,^[28] rare-earth (RE) metal complexes can act as Lewis acids. [RE(OTf)₃] (OTf: trifluoromethanesulfonyl) compounds are known as water-compatible catalysts.^[29] However, these catalysts exhibit low activity or require long reaction times.

The Michael reaction of **1a** with **2b** was carried out under aqueous conditions using various Mⁿ⁺-monts and the results are summarized in Table 4. No reaction occurred in the absence of the catalyst (Table 4, entry 8). As expected, Mⁿ⁺-monts having RE³⁺ metal cations were effective within 0.5 h (Table 4, entries 1–4); the Sc³⁺-mont gave the highest yield

Table 4. Michael reaction of ethyl 2-oxo-cyclopentanecarboxylate (**1a**) with 3-buten-2-one (**2b**) using various catalysts.^[a]

Entry	Catalyst	Yield ^[b] [%]
1	Sc ³⁺ -mont	99
2	Yb ³⁺ -mont	83
3	Yb ³⁺ -mont	62
4	La ³⁺ -mont	62
5	Cu ²⁺ -mont	17
6	Zn ²⁺ -mont	16
7	[Sc(OTf) ₃]	7
8	no	0

[a] Reaction conditions; active metal species (0.04 mmol), **1a** (2 mmol), **2b** (2.2 mmol), water (3 mL), 30°C, 0.5 h. [b] Yields of **3b** were determined by GC based on donor.

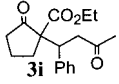
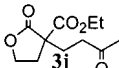
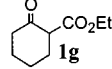
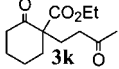
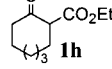
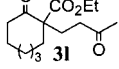
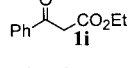
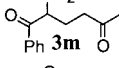
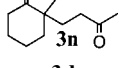
of ethyl 2-oxo-1-(3-oxobutyl)-cyclopentanecarboxylate (**3b**) (Table 4, entry 1) and exhibited significantly higher catalytic activity than that of the homogeneous Sc(OTf)₃ (Table 4, entry 7).^[30]

In contrast, the catalytic activities of Cu²⁺- and Zn²⁺-monts under similar conditions were extremely low (Table 4, entries 5 and 6). A similar phenomenon is also observed for Mukaiyama–aldol reactions using various metal salts under aqueous conditions.^[20]

Generally, treatment of RE³⁺ metal triflates with water gives RE³⁺ aqua complexes surrounded by low nucleophilic OTf counteranions in the second coordination sphere, which act as Lewis acids.^[31] Yb salts with low nucleophilic counteranions such as OTf[−] and ClO₄[−] catalyze the aldol reaction of silyl enol ethers with aldehydes in aqueous media, whereas combining Yb salts with Cl[−], OAc[−], NO₃[−], and SO₄^{2−} ions results in low catalytic activity.^[33] Elemental analysis of the Sc³⁺-mont revealed an absence of OTf groups in the mont catalyst. Additionally, Sc/Al₂O₃ and Sc/SiO₂ were completely inactive for Michael reactions. Presumably, Sc³⁺ aqua complexes partnered with anionic silicate layers of monts, whose negative charge is delocalized along the layer,^[7,33] would provide an outstanding catalytic activity.

Under aqueous conditions, Sc³⁺-mont-catalyzed Michael reactions were extended to other 1,3-dicarbonyl substrates (Table 5). In all cases, the reaction proceeded smoothly in

Table 5. Michael reaction of various 1,3-dicarbonyl compounds with enones catalyzed by Sc³⁺-mont in water.^[a]

Entry	Donor	Acceptor	Product	Temp. [°C]	Time [h]	Yield ^[b] [%]
1	1a	2b	3b	30	0.5	99
2 ^[c]	1a	2b	3b	30	0.5	99
3 ^[d]	1a	2b	3b	30	0.5	99
4 ^[e]	1a	2b	3b	30	0.5	99
5	1b	2b	3c	50	2	90
6	1a	2c	3f	30	1	98
7	1a			50	1	90
8		2b		50	2	99
9		2b		45	3	99
10 ^[f]		2b		60	2	80
11		2b		50	2	97
12		2b		50	1	96
13	1c	2b	3d	45	3	98
14	1d	2b	3e	50	1	97

[a] Reaction conditions; Sc³⁺-mont (Sc: 0.04 mmol), donor (2 mmol), acceptor (2.2 mmol), H₂O (3 mL). [b] Yields of products were determined by GC based on donor. [c] Reuse-1. [d] Reuse-2. [e] Reuse-3. [f] Sc³⁺-mont (Sc: 0.02 mmol), **1h** (0.5 mmol), **2b** (0.55 mmol), H₂O (1 mL).

the presence of 2–4 mol% Sc catalyst within 3 h to afford the corresponding Michael adducts in excellent yields. Hydrolysis of the ester moieties did not occur (Table 5, entries 1–11). Recently, heterogeneous Michael reactions in water using organic polymer-supported^[4j,m] and surfactant-combined^[34] Sc catalysts as Lewis acids have been reported. These systems have the drawback of waste production because activated donors such as silyl enol ethers or 1.5–3 equivalents of acceptor are required. The Sc³⁺-mont overcomes these limitations and is the most active Lewis acid catalyst for the Michael reaction of 1,3-dicarbonyl compounds with enones using water as a solvent. Importantly, even after three recycling experiments, no appreciable loss of catalytic activity and selectivity occurred. For reaction of **1a** with **2b**, 99% yields for **3b** were obtained during three recycling experiments (Table 5, entries 2–4). The used catalyst retained its original Sc content as confirmed by elemental analysis. The stability of the [Sc(H₂O)₆]³⁺ species in the recovered Sc³⁺-mont catalyst was established by XAFS measurement, as shown in Figure 3 and Table 1.

Application of the Cu²⁺-mont catalyst to Sakurai–Hosomi and Diels–Alder reactions: To explore the catalytic activity of Cu²⁺-mont as a Lewis acid, it was applied to the Sakurai–Hosomi reaction, that is the allylation of carbonyl compounds with allylsilanes, which is of great interest in organic chemistry because of the synthetic utility of homoallylic alcohols.^[35] The catalytic activity in the reaction of benzaldehyde (**4a**) with allyltrimethylsilane (**5**) under solvent-free conditions was compared with that of many other copper catalysts; typical results are displayed in Table 6. Among the

silyl ether **6a**, was detected. We explored the simple and efficient proton-mediated desilylation to homoallylic alcohols. After complete conversion of **4a**, ethanol was added and the reaction mixture was stirred at 80 °C for 1 h to afford **7a** in 99% yield.^[36]

One-pot syntheses of various homoallylic alcohols were performed by using the Cu²⁺-mont catalyst, as exemplified in Table 7. A variety of aldehydes and ketones reacted

Table 7. Allylation of carbonyl compounds with allyltrimethylsilane (**5**).^[a]

$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 + \text{CH}_2=\text{CH}-\text{SiMe}_3 \xrightarrow[2)]{1)} \text{R}^1-\text{C}(\text{OH})(\text{CH}_2\text{CH}=\text{CH}_2)-\text{R}^2$						
Entry	Carbonyl compound	5 [equiv]	Product	Temp. ^[b] [°C]	Time ^[b] [h]	Yield ^[c] [%]
1	4a	1.1	7a	45	1	99
2	4b	1.5	7b	45	1	97
3 ^[d]	4c	1.5	7c	RT	6	95
4 ^[d]	4d	1.5	7d	RT	1	90
5 ^[d]	4e	2	7e	40	2	80
6 ^[d]	4f	2	7f	55	3	81

[a] Reaction conditions; 1) Cu²⁺-mont (Cu: 0.05 mmol), **4a–f** (4 mmol), **5** (1.1–2 equiv), 2) EtOH (1 mL), 80 °C, 1 h. [b] For the allylation reaction (1). [c] Yields of products were determined by GC based on carbonyl compound. [d] Nitromethane (3 mL) was used as the solvent.

Table 6. Allylation reaction of benzaldehyde with allyltrimethylsilane using various Cu catalysts.^[a]

$\text{Ph}-\text{C}(=\text{O})-\text{H} + \text{CH}_2=\text{CH}-\text{SiMe}_3 \xrightarrow[45^\circ\text{C}, 1\text{ h}]{\text{Cu catalyst}} \text{Ph}-\text{C}(\text{OSiMe}_3)(\text{CH}_2\text{CH}=\text{CH}_2) + \text{Ph}-\text{C}(\text{OH})(\text{CH}_2\text{CH}=\text{CH}_2)$			
Entry	Catalyst	Yield of (6a + 7a) ^[b] [%]	
1	Cu ²⁺ -mont	99	
2	Cu ²⁺ -hydrotalcite	0	
3	Cu ²⁺ -zeolite-(X)	0	
4	Cu/Al ₂ O ₃	0	
5	Cu/SiO ₂	0	
6	Cu(NO ₃) ₂ ·3H ₂ O	0	

[a] Reaction conditions; catalyst (Cu: 0.05 mmol), **4a** (4 mmol), **5** (6 mmol), 45 °C, 1 h. [b] Yields of products were determined by GC based on **4a**.

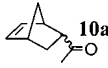
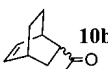
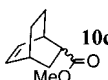
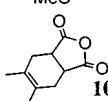
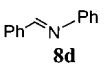
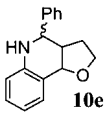
Cu catalysts tested, the Cu²⁺-mont possessed the greatest activity (99% yield after 1 h, Table 6, entry 1) to afford trimethyl[(1-phenyl-3-butenyl)oxy]silane (**6a**) and 4-phenyl-1-buten-4-ol (**7a**) in 98 and 1% yields, respectively. In contrast, the allylation reaction hardly occurred in the presence of Cu²⁺-hydrotalcite, Cu²⁺-zeolite-(X), Cu/Al₂O₃, Cu/SiO₂, and Cu(NO₃)₂·3H₂O (Table 6, entries 2–6).

In the above reaction, a small amount of the homoallylic alcohol **7a**, which is formed by hydrolysis of the homoallyl

smoothly with **5** to give the corresponding homoallylic alcohols. Cyclic and linear aliphatic aldehydes, as well as ketones, required nitromethane as a solvent to obtain the desired products in high yields. The recovered catalysts showed comparable activity and selectivity with fresh ones. Yields of the homoallylic alcohol remained at 99%, while the catalysts were recycled three times. A 100-mmol-scale reaction of **4a** with **5** in the presence of the Cu²⁺-mont catalyst afforded **7a** in 86% yield. In contrast to previously reported homogeneous aluminum bis(trifluoromethylsulfonyl)amides,^[37] ytterbium trichlorides,^[38] trimethylsilylmethane sulfonates,^[39] indium trichloride/chlorotrimethylsilane,^[40] and heterogeneous Al- and K-10 montmorillonites,^[41] the Cu²⁺-mont catalyst system is nonpolluting and recyclable, and eliminates halogenated reagents and solvents.

The Cu²⁺-mont catalyst also promoted Diels–Alder reactions under solvent-free conditions (Table 8). For example, the reaction between 1,3-cyclohexadiene (**8b**) and **2b** produced 2-acetylbicyclo[2.2.2]oct-5-ene (**10b**) in 99% yield (Table 8, entry 2). A control experiment confirmed that a trace of **10b** formed without catalyst under identical reaction conditions. The imino Diels–Alder reaction of benzylideneaniline (**8d**) with 2,3-dihydrofuran (**9c**) also proceeded

Table 8. Cu²⁺-mont-catalyzed Diels–Alder reaction.^[a]

Entry	Diene	Dienophile	Product	Temp. [°C]	Time [h]	Yield ^[b,c] [%]
1		2b		40	1	99(90/10)
2		2b		40	1	97(99/1)
3	8b			40	1	95(90/10)
4 ^[d]				40	0.5	90
5 ^[e]				50	4	85(54/46) ^[f]

[a] Reaction conditions; Cu²⁺-mont (Cu: 0.05 mmol), **8a** and **8b** (4.4 mmol), **2b** and **9a** (4 mmol). [b] Yields of products were determined by GC based on dienophile. [c] Values in parentheses were *endo/exo* ratio determined by ¹H NMR. [d] **8c** (2 mmol), **9b** (3 mmol). [e] **8d** (1 mmol), **9c** (3 mmol). [f] *cis/trans* ratio.

to give the tetrahydroquinoline derivative (**10e**) in a high yield (Table 8, entry 5). Dimerization of dienes was not observed.

Reaction mechanism for the Cu²⁺-mont-catalyzed Michael reactions: Transition-metal and rare-earth metal catalysts have been extensively used for the Michael reaction of 1,3-dicarbonyl compounds with enones.^[21d] For Ni²⁺, Cu²⁺, Co²⁺, Fe³⁺, and Sc³⁺, the reaction mechanism is considered to involve a ternary complex, in which both the 1,3-dicarbonyl compound and the enone are coordinated to a Lewis acid metal center.^[21d]

A shift in the IR spectrum of the coordinated ketone is a measure of the Lewis acid strength of metal cations.^[42] The $\nu(\text{CO})$ band of cyclopentanone adsorbed onto the Cu²⁺-mont appeared in the IR spectrum at 1685 cm⁻¹, which is lower than that of the free cyclopentanone (1751 cm⁻¹). This shift of 66 cm⁻¹ was larger than those found for the Sc³⁺-, Y³⁺-, Yb³⁺-, and La³⁺-monts (34 cm⁻¹), demonstrating that the Cu²⁺-mont catalyst possesses significantly stronger Lewis acid strength than the other Mⁿ⁺-monts. Yields of the Michael adduct increased with increasing Lewis acid strength of the metal cation (Table 2). Thus, it is reasonable that the Lewis acid sites of Mⁿ⁺-monts play an important role in these carbon–carbon bond-forming reactions. Presumably, the silicate layers of the monts may act as a macro-anion with low nucleophilicity, leading to the formation of a cationic copper center with extremely strong Lewis acidity.

As seen in Figure 4b, upon treatment of the Cu²⁺-mont with 2-cyclohexen-1-one (**2a**), the IR spectrum contained a $\nu(\text{CO})$ band at 1658 cm⁻¹, ascribed to **2a** coordinated to the copper Lewis acid site. Addition of acetylacetone (**1c**) as a donor gave new peaks at 1580, 1558, and 1539 cm⁻¹, as-

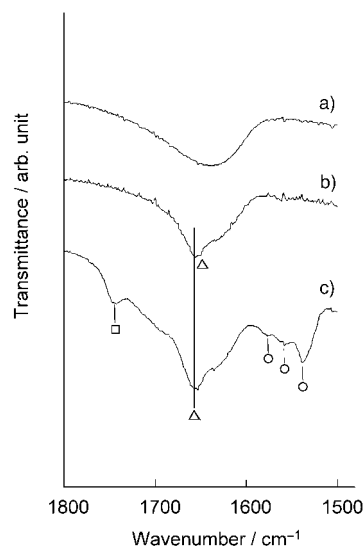
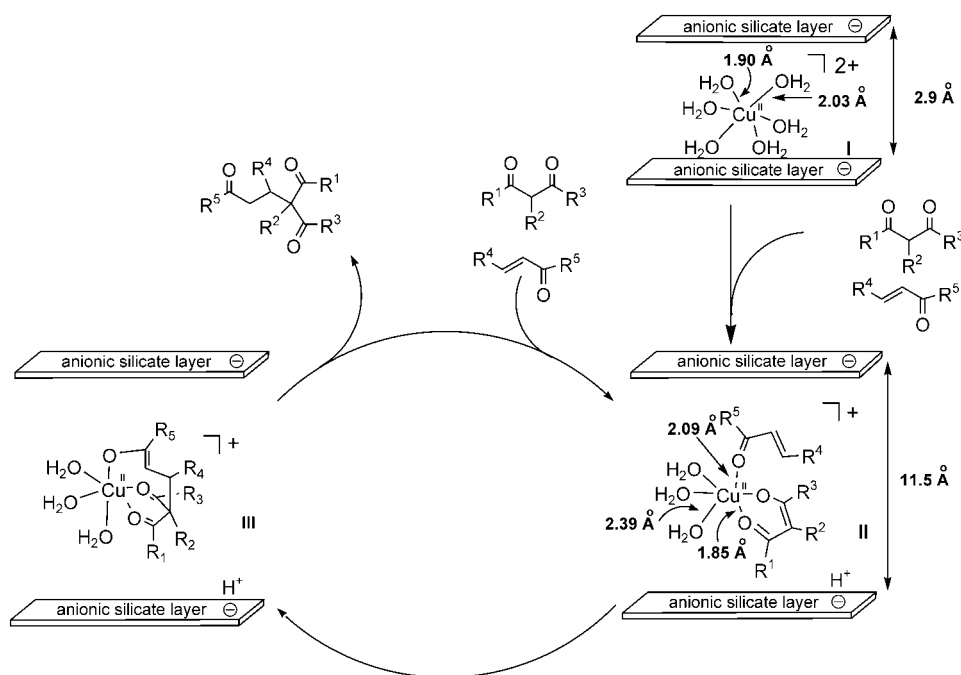


Figure 4. IR spectra of a) fresh Cu²⁺-mont, b) the Cu²⁺-mont after treatment with **2a**, and c) the Cu²⁺-mont after treatment with both **2a** and **1c**. Δ: coordinated **2a** (1658 cm⁻¹); ○: acetylacetonato-Cu species (1580, 1558, and 1539 cm⁻¹, ref. [43]); □: free **1c** (1747 cm⁻¹). The fresh Cu²⁺-mont (0.2 g) was treated with **2a** (1.0 equiv Cu) in nitromethane (1 mL). The **2a**-covered Cu²⁺-mont was further reacted with one equivalent of **1c**.

signed to the acetylacetonato–copper species (○ in Figure 4c).^[43] EXAFS analysis of the same sample supported the generation of two Cu–O bonds 1.86 Å in length and one Cu–O bond 2.60 Å in length, along with the loss of three H₂O ligands from the original Cu²⁺-mont (Table 1). On the basis of these results, it is reasonable that the Cu²⁺-mont-catalyzed Michael reactions involve the ternary copper complex **II**, in which both the 1,3-dicarbonyl compound and the enone coordinate to the Cu²⁺ center (Scheme 3).^[44] The carbon–carbon bond formation produces a Cu-alcoholate intermediate **III**, followed by protolysis to afford the Michael adduct together with regeneration of the original Cu species **I**. The same reaction mechanism has been proposed for the Sc³⁺-mont-catalyzed Michael reactions in water.^[9f] Notably, Michael reactions of nitriles such as ethyl cyanoacetate and malononitrile as donors instead of 1,3-dicarbonyl compounds barely proceeded under these conditions. It is likely that such nitrile compounds strongly coordinate to copper and prevent the interaction of the enones with the Cu complexes. It seems that the Lewis acid site originating from the Cu²⁺ aqua species induces both Sakurai–Hosomi and Diels–Alder reactions by coordination of carbonyl compounds.

One of the important characteristics of montmorillonites is the enlargement of the interlayer distance that occurs in solvents. Indeed, the interlayer space of the Cu²⁺-mont was expanded from 2.9 to 11.5 Å when soaked in a mixture of **1c** and **2a** under solvent-free conditions, as confirmed by XRD.^[45] The efficient catalysis by the Cu²⁺-mont under solvent-free conditions could be related to the expansion of the interlayer space as well as the strong Lewis acid nature of the aqua Cu²⁺ ion enwrapped in the mont interlayer.



Scheme 3. Proposed mechanism for Michael reaction using the Cu^{2+} -mont catalyst.

Conclusion

Montmorillonite-enwrapped copper and scandium aqua complexes have been developed as extremely active and versatile Lewis acid catalysts that can be applied to a variety of carbon–carbon bond-forming reactions under solvent-free or aqueous conditions. The remarkable activity of the mont catalysts is attributable to the negatively charged silicate layers that are capable of stabilizing metal cations. These catalysts are also reusable without any appreciable loss in activity and selectivity.

Experimental Section

General: The following instruments were used in this study: ^1H and ^{13}C NMR (JNM-AL400), IR (JASCO FTIR-410), XRD (Philips X'Pert-MPD), XPS (ESCA-2000), and GLC (Shimadzu GC-8A PF equipped with a flame ionization detector and silicone UC W-98 and OV-1 columns). The interlayer distance was determined by subtracting the c dimension of the silicate sheet (9.6 Å) from the observed d_{001} values in a XRD spectrum.^[16]

The sodium montmorillonite (Na^+ -mont) was supplied by Kunimine Industry Co. Ltd. as Kunipia F (Na 2.69, Al 11.8, Fe 1.46, Mg 1.97 %). $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Sc}(\text{OTf})_3$ were purchased from Wako Pure Chemical and Tokyo Kasei, respectively, and used as received. SiO_2 (JRC-SIO-8) and $\gamma\text{-Al}_2\text{O}_3$ (JRC-ALO-4) were supplied by the Catalyst Society of Japan as reference catalysts. All organic compounds used as substrates and solvents were obtained from Wako Pure Chemical, Tokyo Kasei, Aldrich, or Acros, and purified by standard procedures before use.^[46] The identities of products were confirmed by comparison with reported IR, GC-MS, and ^1H and ^{13}C NMR data.

Preparation of Cu^{2+} -mont catalyst: The Na^+ -mont (3.0 g) was stirred in aqueous $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ($8.3 \times 10^{-3}\text{ M}$, 200 mL) at 50°C for 24 h. The resulting suspension was filtered and the solid was washed repeatedly with

deionized water and dried at 110°C to yield a light blue powder (2.5 g; Cu 3.21 wt %, 0.505 mmol g^{-1}).

Preparation of Sc^{3+} -mont catalyst: The Na^+ -mont (3.0 g) was stirred in aqueous $\text{Sc}(\text{OTf})_3$ ($5.0 \times 10^{-3}\text{ M}$, 200 mL) at 50°C for 24 h. The resulting suspension was filtered, and the solid was washed repeatedly with deionized water, then dried at 110°C to afford a Sc^{3+} -mont as a light gray powder (2.7 g; Sc 1.78 wt %, 0.396 mmol g^{-1}). XPS: Sc $2p_{3/2}$ = 402.6 eV. The XPS peak position is referred to C 1 s at 284.6 eV.

Preparation of mont-enwrapped Y, Yb, La, and Zn cation species: Na^+ -mont (3.0 g) was added to 200 mL of the aqueous solution containing 0.70 g of the corresponding $\text{M}(\text{OTf})_3$, followed by stirring at 50°C for 24 h. After filtration and washing with deionized water, the powder was dried at 110°C to give Y^{3+} -mont (Y, 3.1 wt %), Yb^{3+} -mont (Yb, 4.3 wt %), or La^{3+} -mont (La, 4.5 wt %). Treatment of 3.0 g of the Na^+ -mont with aqueous $\text{Zn}(\text{OTf})_2$ ($1.0 \times 10^{-2}\text{ M}$, 200 mL) followed by filtration, washing, and drying afforded Zn^{2+} -mont (Zn, 6.3 wt %).

Preparation of Cu/SiO_2 and $\text{Cu}/\text{Al}_2\text{O}_3$: SiO_2 (3.0 g) was added to aqueous $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($1.5 \times 10^{-2}\text{ M}$, 100 mL) at 80°C for 24 h. The solid obtained was then dried at 110°C to give Cu/SiO_2 (Cu, 3.2 wt %). The same treatment using Al_2O_3 afforded $\text{Cu}/\text{Al}_2\text{O}_3$ (Cu, 3.2 wt %), which may involve the formation of small clusters of CuO on the Al_2O_3 surface.^[12a]

Preparation of Cu^{2+} -hydrotalcite (Cu-Mg-Al-CO_3): A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (12.9 mmol), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (129.6 mmol), and $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (43.2 mmol) was dissolved in deionized water (120 mL). Then aqueous Na_2CO_3 (120 mL, 0.24 mol) and NaOH (0.39 mol) were slowly added, and the resulting mixture heated at 65°C for 18 h with vigorous stirring. The resulting slurry was filtered, washed with deionized water, and dried at 100°C for 15 h to give 12.0 g of Cu-Mg-Al-CO_3 (Mg 23.4, Al 5.37, Cu 6.4 wt %). The hydrotalcite structure of the gray powder was confirmed by XRD, and had a basal spacing of 7.9 Å, similar to that of the parent Mg-Al-CO_3 hydrotalcite (7.9 Å). The Cu^{2+} species were located within the Brucite-like sheet by isomorphic substitution of Mg^{2+} cation at the octahedral sites.^[47]

Preparation of Cu^{2+} -X zeolite: Copper-ion-exchanged X zeolite (Cu-X) was prepared by treating Na-X zeolite (Wako Pure Chemical), $\text{Na}_{86}(\text{Al}_{86}\text{Si}_{106}\text{O}_{384}) \cdot 264\text{H}_2\text{O}$ ($\text{Si}/\text{Al}=1.23$), with a $1.0 \times 10^{-2}\text{ M}$ aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. The resulting powder was washed with deionized water, dried, and calcined at 300°C to give $\text{Cu-X}^{[10]}$ with a Cu content of 12.0 wt %, which corresponds to 83 % ion exchange of Na^+ . Retention of the crystal structure of the X zeolite was confirmed by XRD. In situ EPR, UV/Vis, and Cu K-edge XANES spectra for the Cu-X indicated dispersed divalent Cu species with a centrosymmetric octahedral coordination environment. Curve-fitting analysis of the k^3 -weighted EXAFS showed that the Cu^{2+} ions displayed Jahn–Teller distorted CuO_6 octahedra with four short Cu–O distances (1.91 Å) and two long Cu–O distances (2.28 Å).

Pretreatment of Cu^{2+} -mont catalyst: Prior to use in C–C bond-forming reactions, the Cu^{2+} -mont was heated under vacuum at 100°C for 2 h in a reaction vessel. Before addition of substrate, the sample was cooled to room temperature under vacuum. This pretreatment is necessary to achieve high catalytic activity and reproducibility of the Michael reaction results. EXAFS studies showed that the local structure of Cu^{2+} ions in the Cu^{2+} -mont did not change appreciably after this treatment. Removal of adsorbed water within the interlayer of mont by the pretreatment

allows access of the substrates to the active Cu^{2+} species enwrapped in the mont.

A typical procedure for the Michael reaction with a Cu^{2+} -mont catalyst under solvent-free conditions: **1a** (4 mmol) and **2a** (4.4 mmol) were added to the pretreated Cu^{2+} -mont (0.09 g, Cu: 0.05 mmol). The heterogeneous reaction mixture was stirred at 70°C for 2 h, and the Cu^{2+} -mont was removed by filtration and washed with acetone and deionized water, followed by drying at 110°C. GC analysis of the filtrate showed 92% yield of **3a**.

Procedure for 100-mmol-scale Michael reaction: **1e** (16.0 g, 100 mmol) was poured onto the pretreated Cu^{2+} -mont catalyst (0.5 g, Cu: 0.253 mmol), followed by addition of **2d** (12.3 g, 150 mmol). After the mixture had been stirred at 100°C for 14 h, the Cu^{2+} -mont was removed by filtration and washed with acetone. The acetone washings were combined and distilled to give **3h** (22.0 g; 91% yield) as a colorless oil.

A typical procedure for the Michael reaction with a Sc^{3+} -mont catalyst in water: A mixture of **1a** (2 mmol), **2b** (2.2 mmol), the Sc^{3+} -mont (0.1 g, Sc: 0.039 mmol), and water (3 mL) was stirred at 30°C under argon. After 0.5 h, the Sc^{3+} -mont was separated by centrifugation and GC analysis of the supernatant showed 99% yield of **3b**. The residual solid catalyst was washed with acetone and reused under identical conditions.

A typical procedure for the Cu^{2+} -mont-catalyzed Sakurai–Hosomi reaction under solvent-free conditions: **4a** (4 mmol) and **5** (4.4 mmol) were added to the Cu^{2+} -mont (0.09 g, Cu: 0.05 mmol). After the mixture had been stirred at 45°C for 1 h, EtOH (1 mL) was added and the mixture allowed to react further at 80°C. The Cu^{2+} -mont was removed by filtration and GC analysis of the filtrate showed 99% yield of **7a**. The isolated catalyst was washed with acetone and deionized water, followed by drying at 110°C. Product yields remained at 99% during three cycles of the reaction using the same catalyst.

Procedure for 100-mmol-scale Sakurai–Hosomi reaction: Compounds **4a** (10.6 g, 100 mmol) and **5** (12.6 g, 110 mmol) were added onto pretreated Cu^{2+} -mont (0.5 g, Cu: 0.253 mmol). After the mixture had been stirred at 50°C for 2 h, EtOH (20 mL) was added to the reaction mixture and it was allowed to react further at 80°C. The Cu^{2+} -mont was removed by filtration and washed with acetone. The combined acetone washings were distilled to afford pure **7a** as a colorless oil (12.7 g, 86%).

Diels–Alder reaction between cyclohexadiene and 3-buten-2-one: **2b** (4 mmol) and **8b** (4.4 mmol) were added to the pretreated Cu^{2+} -mont catalyst (0.09 g, Cu: 0.05 mmol) and the resulting mixture was stirred at 40°C for 1 h. A 99% yield of **10b** (*endo:exo* = 99:1) was confirmed by GC analysis. The *endo:exo* ratio was determined by ^1H NMR spectroscopy.

IR measurements for determination of the ternary complex: The IR spectra of the M^{n+} -monts were obtained at room temperature in transmission mode. The M^{n+} -monts (0.2 g) were treated with one equivalent of a donor relative to the amount of metal cation in nitromethane (1 mL) at room temperature. After removal of the solvent by evaporation at 30°C, the M^{n+} -monts were subsequently treated with an acceptor (1.0 equiv) in the same manner as the donor. In each step, the M^{n+} -monts were pressed into a disk and subjected to IR measurement.

X-ray absorption fine structure (XAFS) measurements: The Cu K-edge X-ray absorption spectra were measured in transmission mode at the EXAFS facilities installed at the BL-7C line of KEK-PF, Tsukuba, Japan (prop. No.2001G143). For details of the data analysis, refer to the reported procedure.^[48] The curve-fitting analysis of reverse FT was conducted by using Cu–O and Sc–O shells with empirical values of back scattering amplitude and phase shift extracted from CuO and Sc_2O_3 , respectively, assuming the peaks originated from scattering by the neighboring oxygen.

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- [1] a) *Lewis Acids in Organic Synthesis* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **2000**; b) *Selectivities in Lewis Acid Promoted Reactions* (Ed.: D. Schinzer), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1989**.
- [2] a) J. H. Clark, *Green Chem.* **1999**, *1*, 1; b) P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, London, **1998**.
- [3] J. H. Clark, *Acc. Chem. Res.* **2002**, *35*, 791.
- [4] For recent representative examples of supported Lewis acids for carbon–carbon bond forming reactions, see: Ag: a) C. Hague, N. J. Patmore, C. G. Frost, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2001**, 2286; Al: b) A. Díaz-Ortiz, A. de la Hoz, A. Moreno, A. Sánchez-Migallón, G. Valiente, *Green Chem.* **2002**, *4*, 339; c) X. Hu, G. K. Chuah, S. Jaenicke, *Appl. Catal. A* **2001**, *217*, 1; d) T. Nishimura, S. Ohtaka, A. Kimura, E. Hayama, Y. Haseba, H. Takeuchi, S. Uemura, *Appl. Catal. A* **2000**, *194–195*, 415; B: e) Y. Qin, G. Cheng, A. Sundararaman, F. Jäkle, *J. Am. Chem. Soc.* **2002**, *124*, 12672; Bi: f) B. M. Choudary, Ch. Sridhar, M. Sateesh, B. Sreedhar, *J. Mol. Catal. A Chem.* **2004**, *212*, 237; Fe: g) B. M. Khadilkar, S. D. Borkar, *Tetrahedron Lett.* **1997**, *38*, 1641; RE (rare earth): h) P. Sreekanth, S.-W. Kim, T. Hyeon, B. M. Kim, *Adv. Synth. Catal.* **2003**, *345*, 936; i) J. Perles, M. Iglesias, C. R. Valero, N. Sneijko, *Chem. Commun.* **2003**, 346; j) W. Gu, W.-J. Zhou, D. L. Gin, *Chem. Mater.* **2001**, *13*, 1949; k) M. T. Reetz, D. Giebel, *Angew. Chem.* **2000**, *112*, 2614; *Angew. Chem. Int. Ed.* **2000**, *39*, 2498; l) S. Nagayama, S. Kobayashi, *Angew. Chem.* **2000**, *112*, 578; *Angew. Chem. Int. Ed.* **2000**, *39*, 567; m) R. Anwender, H. W. Görlitzer, G. Gerstberger, C. Palm, O. Runte, M. Spiegler, *J. Chem. Soc. Dalton Trans.* **1999**, 3611; n) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1998**, *120*, 2985; o) H. Kotsuki, K. Arimura, *Tetrahedron Lett.* **1997**, *38*, 7583; Sn: p) A. Corma, M. Renz, *Chem. Commun.* **2004**, 550; q) T. M. Jyothi, M. L. Kaliya, M. V. Landau, *Angew. Chem.* **2001**, *113*, 2965–2968; *Angew. Chem. Int. Ed.* **2001**, *40*, 2881–2884; Zn: r) J. Liu, D. Yin, D. Yin, Z. Fu, Q. Li, G. Lu, *J. Mol. Catal. A Chem.* **2004**, *209*, 171; Zn/Fe: s) B. M. Khadilkar, S. D. Borkar, *J. Chem. Technol. Biotechnol.* **1998**, *71*, 209.
- [5] For reviews on solvent-free organic synthesis, see: a) G. W. V. Cave, C. L. Raston, J. L. Scott, *Chem. Commun.* **2001**, 2159; b) K. Tanaka, F. Toda, *Chem. Rev.* **2000**, *100*, 1025; c) J. O. Metzger, *Angew. Chem.* **1998**, *110*, 3145; *Angew. Chem. Int. Ed.* **1998**, *37*, 2975;
- [6] a) *Organic Synthesis in Water* (Ed.: P. A. Grieco), Blackie Academic and Professional, London, **1998**; b) C.-J. Li, T.-H. Chan, *Organic Reactions in Aqueous Media*, Wiley, New York, **1997**.
- [7] a) P. Laszlo, *Science* **1987**, *235*, 1473; b) T. J. Pinnaiva, *Science* **1983**, *220*, 365.
- [8] Excellent reviews of mont-catalyzed organic syntheses: a) J. H. Clark, D. J. Macquarrie, *Chem. Soc. Rev.* **1996**, *25*, 303; b) Y. Izumi, M. Onaka, *Adv. Catal.* **1992**, *38*, 245; c) P. Laszlo, *Acc. Chem. Res.* **1986**, *19*, 121.
- [9] Ti: a) T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* **2003**, *44*, 9205; b) T. Kawabata, M. Kato, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Lett.* **2003**, *32*, 648; c) T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, *Tetrahedron Lett.* **2001**, *42*, 8329; d) K. Ebitani, T. Kawabata, K. Nagashima, T. Mizugaki, K. Kaneda, *Green Chem.* **2000**, *2*, 157; Fe: e) K. Ebitani, M. Ide, T. Mitsudome, T. Mizugaki, K. Kaneda, *Chem. Commun.* **2002**, 690; Sc: f) T. Kawabata, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2003**, *125*, 10486.
- [10] K. Ebitani, K. Nagashima, T. Mizugaki, K. Kaneda, *Chem. Commun.* **2000**, 869.

- [11] G. F. McCann, G. J. Millar, G. A. Bowmaker, R. P. Cooney, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 4321.
- [12] a) T. Yamamoto, T. Tanaka, R. Kuma, S. Suzuki, F. Amano, Y. Shimooka, Y. Kohno, T. Funabiki, S. Yoshida, *Phys. Chem. Chem. Phys.* **2002**, *4*, 2449; b) L.-S. Kau, D. J. Spira-Solomon, J. E. Penner-Harn, K. O. Hodgson, E. I. Solomon, *J. Am. Chem. Soc.* **1987**, *109*, 6433.
- [13] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., Wiley, New York, **1988**, p. 755.
- [14] C. Lamberti, G. Spoto, D. Scarano, C. Pazé, M. Salvalaggio, S. Bordiga, A. Zecchina, G. T. Palomino, F. D'Acapito, *Chem. Phys. Lett.* **1997**, *269*, 500.
- [15] H. Ohtaki, M. Maeda, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2197.
- [16] M. B. McBride, T. J. Pinnavaia, M. M. Mortland, *J. Phys. Chem.* **1975**, *79*, 2430.
- [17] J. M. Harrowfield, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1994**, *47*, 397.
- [18] Y. Ohni, Y. Suzuki, T. Takeguchi, A. Ouchi, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 393.
- [19] G. R. Willey, P. R. Meehan, M. D. Rudd, M. G. B. Drew, *J. Chem. Soc. Dalton Trans.* **1995**, 3175.
- [20] S. Kobayashi, S. Nagayama, T. Busujima, *J. Am. Chem. Soc.* **1998**, *120*, 8287.
- [21] a) T.-L. Ho, *Tactics of Organic Synthesis*, Wiley, New York, **1994**; b) M. E. Jung in *Comprehensive Organic Synthesis*, Vol. 4, (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 1; c) H. O. House, *Modern Synthetic Reactions*, 2nd ed., Benjamin, Menlo Park, Calif., **1972**, p. 595; d) For an excellent review on transition-metal-catalyzed Michael reaction of 1,3-dicarbonyl compounds, see: J. Christoffers, *Eur. J. Org. Chem.* **1998**, 1259.
- [22] High activities were also obtained for the Cu^{2+} -mont catalysts prepared using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and $\text{Cu}(\text{OTf})_2$ instead of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.
- [23] Lewis acid strength of metal salts was evaluated from the g_{zz} values of ESR spectra of superoxide metal ion complexes (Sc 1.00; Y 0.85; Yb 0.83; La 0.82; Zn 0.71; Na 0.34). See: a) S. Fukuzumi, K. Ohkubo, *J. Am. Chem. Soc.* **2002**, *124*, 10270; b) S. Fukuzumi, K. Ohkubo, *Chem. Eur. J.* **2000**, *6*, 4532.
- [24] J. Christoffers, *Chem. Commun.* **1997**, 943.
- [25] A. C. Coda, G. Desimoni, P. Righetti, G. Tacconi, *Gazz. Chim. Ital.* **1984**, *114*, 417.
- [26] S. Matsunaga, T. Ohshima, M. Shibasaki, *Adv. Synth. Catal.* **2002**, *344*, 3, and references therein.
- [27] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2003**, *125*, 11460.
- [28] C. F. Baes, Jr., R. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, **1976**.
- [29] S. Kobayashi, M. Sugiura, H. Kitagawa, W. W.-L. Lam, *Chem. Rev.* **2002**, *102*, 2227.
- [30] For a review see: S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15.
- [31] S. Kobayashi, K. Manabe, *Acc. Chem. Res.* **2002**, *35*, 209.
- [32] S. Kobayashi, I. Hachiya, *J. Org. Chem.* **1994**, *59*, 3590.
- [33] M. Onaka, *Yuki Gosei Kagaku Kyokaiishi* **1995**, *53*, 392.
- [34] Y. Mori, K. Kakumoto, K. Manabe, S. Kobayashi, *Tetrahedron Lett.* **2000**, *41*, 3107.
- [35] a) J. A. Marshall, *Chem. Rev.* **1996**, *96*, 31; b) Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207; c) A. Hosomi, *Acc. Chem. Res.* **1988**, *21*, 200.
- [36] Notably, a mont-enwrapped titanium (Ti^{4+} -mont)^[9a-d] can be used in the absence of ethanol for the desilylation to homoallylic alcohols even at 50 °C.
- [37] A. Marx, H. Yamamoto, *Angew. Chem.* **2000**, *112*, 182; *Angew. Chem. Int. Ed.* **2000**, *39*, 178;
- [38] X. Fang, J. G. Watkin, B. P. Warner, *Tetrahedron Lett.* **2000**, *41*, 447.
- [39] M. W. Wang, Y. J. Chen, D. Wang, *Synlett* **2000**, 385.
- [40] Y. Onishi, T. Ito, M. Yasuda, A. Baba, *Eur. J. Org. Chem.* **2002**, 1578.
- [41] M. Kawai, M. Onaka, Y. Izumi, *Chem. Lett.* **1986**, 381.
- [42] a) A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature* **2001**, *412*, 423; b) A. Corma, M. E. Domine, L. Nemeth, S. Valencia, *J. Am. Chem. Soc.* **2002**, *124*, 3194.
- [43] a) J. W. Carmichael, Jr., L. K. Steinrauf, R. L. Belford, *J. Chem. Phys.* **1965**, *43*, 3959; b) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., pt. B, Wiley, New York, **1997**, p. 91.
- [44] J. Christoffers, *Chem. Eur. J.* **2003**, *9*, 4862.
- [45] The interlayer distance of the Sc^{3+} -mont was also expanded from 3.6 Å to 11.4 Å. In water, the interlayer space of the Cu^{2+} -mont was 7.0 Å, which is smaller than that of the Sc^{3+} -mont (8.3 Å).
- [46] *Purification of Laboratory Chemicals*, 3rd ed. (Eds.: D. D. Perrin, W. L. F. Armarego), Pergamon, Oxford, **1988**.
- [47] M. Köckerling, G. Geismar, G. Henkel, and H.-F. Nolting, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 481.
- [48] T. Tanaka, H. Yamashita, R. Tsuchitani, T. Funabiki, S. Yoshida, *J. Chem. Soc. Faraday Trans.* **1988**, *84*, 2987.

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