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Supporting Information

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

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The synthesis of montmorillonite-enwrapped Sc catalysts: A 3.0 g of Na⁺-mont (Kunipia F, Kunimine Industry Co. Ltd.) was stirred in a 200 mL of 5.0 × 10⁻³ M aqueous Sc(OTf)₃ solution at 50 °C for 24 h. The resulting suspension was filtered, and the solid was repeatedly washed with deionized water, then dried at 110 °C to afford a Sc³⁺-mont as a light gray powder (Sc content: 0.396 mmol g⁻¹).

A typical procedure for the Michael reaction with Sc³⁺-mont catalyst in water: A mixture of ethyl 2-oxocyclopentanecarboxylate **1a** (2 mmol), freshly distilled 3-buten-2-one **2a** (2.2 mmol), the Sc³⁺-mont (0.1 g, Sc: 0.039 mmol), and water (3 mL) was stirred at 30 °C. After 1 h, the Sc³⁺-mont was separated by centrifugation and GC analysis of the supernatant showed 99 % yield of ethyl 2-oxo-1-(3-oxobutyl) cyclopentanecarboxylate **3a**. The residual solid catalyst was washed with acetone and subjected to the re-use experiment under identical conditions. The first, the second, and the third runs gave **3a** in 99, 98, and 99 % GC yields, respectively. ICP analysis of the filtrate after the reaction of **1a** with **2a** revealed that the amount of leached Sc was less than 0.1 % with respect to the Sc loading of the Sc³⁺-mont.

A typical procedure for the Sc³⁺-mont-catalyzed Michael reaction under solvent-free conditions: Into a reaction vessel was placed the Sc³⁺-mont (0.1 g, Sc: 0.039 mmol), and heated under an Ar stream at 195 °C for 2 h. After cooling, **1a** (4 mmol) was poured onto the catalyst, followed by the addition of **2a** (4.4 mmol). The reaction mixture was stirred at 50 °C for 1 h and the Sc³⁺-mont was removed by filtration and washed with acetone. GC analysis of the filtrate showed 98 % yield of **3a**.

The isolated catalyst was washed with acetone and deionized water, followed by drying at 110 °C. The yield of **3a** could be kept over 97 % during three times recycling of the catalysts.

A procedure of the 100 mmol-scale Michael reaction of 1a with 2a: Into a reaction vessel was placed the Sc³⁺-mont (0.2 g, Sc: 0.078 mmol), and heated under an Ar stream at 195 °C for 2 h. After cooling, **1a** (15.6 g, 100 mmol) was poured onto the catalyst, followed by the addition of **2a** (10.5 g, 150 mmol). After the reaction mixture was stirred at 50 °C for 2 h, the Sc³⁺-mont was removed by filtration and washed with acetone. The combined mixture was distilled to give 20.5 g (91 % yield) of **3a** as an colorless oil: bp 151-152 °C / 6 mmHg.

Characterization of the Sc³⁺-mont by Sc K-edge X-ray absorption fine structure (XAFS): X-ray absorption spectra were measured in a transmission mode at the EXAFS facilities installed at BL-9A line of KEK-PF, Tsukuba, Japan (prop. No.2001 G143). Details of data analysis are referred to the reported procedure; see Tanaka, T.; Yamashita, H.; Tsuchitani, R.; Funabiki, T.; Yoshida, S. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 2987. Results of curve-fitting analysis for Sc³⁺-mont are as shown in Table 3 and Figure 1. Inverse Fourier transformations were performed for the region of 1.25-2.15 Å.

Table 3. Curve-Fitting Analysis of the Sc-O shell for Sc³⁺-mont Catalysts

sample	<i>R</i> (Å) ^a	C. N. ^b	$\Delta \sigma$ (Å ²) ^c
Sc ³⁺ -mont (A)	2.13	6.0	0.0019
Recovered Sc ³⁺ -mont (B)	2.13	6.1	0.0014

^a*R*: Interatomic distance ^bC. N.: Coordination number. ^c $\Delta \sigma$ is the difference between the Debye-Waller factor of Sc³⁺-mont and that of the reference sample.

Figure 1. FT magnitude of k^3 -weighted EXAFS of (a) Sc^{3+} -mont, (c) recovered Sc^{3+} -mont for the Michael reaction of **1a** with **2a**, inverse FT of the peaks with the $1.25 < R/\text{Å} < 2.15$ range (b) in part a, and (d) in part c. The dotted lines in part b and part d show the result of a curve-fitting analysis using a Sc-O shell parameter in the range 4-10 Å⁻¹.

Effect of solvent: Michael reactions of **1a** with **2a** in various solvents were carried out in the presence of the Sc^{3+} -mont. The results are summarized in Table 4.

Table 4. Effect of Solvent on the Michael Reaction of **1a** with **2a**^a

entry	solvent	yield of 3a ^b (%)
1	water	98
2	acetonitrile	95
3	nitromethane	91
4	toluene	45
5	1,2-dichloroethane	44
6	<i>n</i> -hexane	26
7	THF	10
8	DMA	0

^aReaction conditions: Sc^{3+} -mont (0.1 g, Sc : 0.04 mmol), **1a** (2 mmol), **2a** (2.2 mmol), solvent (3 mL), 30 °C, 0.5 h. ^bDetermined by GC based on **1a**.

Scope of Michael donor: Concerning the scope of the Michael donors besides 1,3-dicarbonyl compounds, we have tried the reactions of nitriles such as ethyl cyanoacetate and malononitrile as donors. However, the above reactions hardly proceeded in the present conditions. Presumably, formation of a 1,3-dionato Sc complex might play an important role in the Sc^{3+} -mont-catalyzed Michael reactions.