

論文の内容の要旨

非積層化モンモリロナイトに包含された
スズ及びチタン水酸化物／酸化物ナノ粒子から成る
新規多孔性粘土触媒の開発
(Development of Novel Porous Clay Catalysts
Composed of Delaminated Montmorillonite-embedded
Tin or Titanium Hydroxide/Oxide Nanoparticles)

氏名 竹平 悟市

1. Introduction

Montmorillonite (Mont) is a naturally-occurring clay composed of laminated anionic aluminosilicate unit layers (Mont layers) intercalating alkali/alkaline-earth metal ions such as Na^+ and Ca^{2+} . Treatment of the natural Mont with aq. solutions of multivalent metal (M) salts affords M-Monts which often show marvelous solid acid catalysis. We originally prepared Sn-Mont upon treatment of the natural Na-Mont with aq. SnCl_4 , and unveiled its unique structure composed of tin hydroxide nanoparticles surrounded by delaminated Mont layers, as well as the efficient acid catalysis for the reactions such as the allylation, cyanation and reduction of alcohols, the Strecker reactions and cyanosilylation of ketones, and lactate synthesis from trioses.¹ Sn-Mont has a unique pore structure that shallow microporous areas where active acid sites lie are directly connected to mesoporous ones, leading to the efficient material transport of reactants and products. In contrast, the laminated structures of Mont layers are found in not only conventional M-Monts but also pillared clays (PILC) which have thermo-stable metal oxide pillars permanently keeping the layers apart in a parallel fashion.

In my Ph.D. study, initially I demonstrated the utility of Sn-Mont as a solid acid catalyst for the reactions involving bulky substrates, and also revealed the crucial factors causing the formation of tin hydroxide and the delamination of Mont layers during the synthesis of Sn-Mont. Furthermore, I developed a novel titanium (hydr)oxide-embedded montmorillonite in which titanium (hydr)oxide nanoparticles are surrounded by delaminated Mont layers, resembling Sn-Mont, and demonstrated its efficiency in some acid-catalyzed reactions.

2. The Mukaiyama aldol reactions for congested ketones catalyzed by tin hydroxide-embedded montmorillonite

The Mukaiyama aldol reactions are acid-promoted additions of silicon enolates to carbonyl acceptors, most of which are aldehydes. On the other hand, the use of less reactive ketones is limited as an acceptor because the additions to ketones are much more sluggish than those to aldehydes. In fact, based on my calculations, ΔG for the Mukaiyama aldol

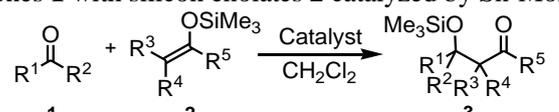
reaction of acetone with its silicon enolate had a less negative value than that of acetaldehyde and the corresponding ΔG^\ddagger was greater as well. Interestingly, the reactions of 2-acetonaphthone (**1b**) and nonan-5-one (**1c**) with a silicon enolate from ketone **2a** afforded the corresponding products **3ba** and **3ca** in excellent yields (Table 1). No reaction with benzophenone (**1e**) took place as predicted by $\Delta G > 0$ based on my calculation, while that with more reactive *p*-chlorobenzophenone (**1f**) was successful. It is well known that the silicon enolates of esters are more nucleophilic than those of ketones, and the calculated ΔG for the reaction of acetone with an ester enolate had a greater negative value than that of a ketone enolate and the corresponding ΔG^\ddagger was smaller. In fact, the reactions of ketones **1a–1e** with ester enolate **2b** afforded the corresponding silylated aldol products in excellent yields. Cyclic enolate **2c**, more congested enolate **2d** and thioester enolate **2e** were also applicable.

3. Different formation mechanisms for Sn-Mont and other multivalent metal ions-exchanged montmorillonites and their determinants

I presumed that the intrinsic structures of M-Mont were determined by the following two factors; whether or not polynuclear metal hydroxides were easily formed between the Mont layers, and whether or not the Mont layers were completely delaminated during the ion-exchange process. In my previous study, it was revealed that the structural diversity of M-Monts mainly depended on the kind of metal species M included. For example, Al-Mont has mononuclear aluminum cations intercalated between laminated Mont layers, Fe-Mont and Ti-Mont are composed of the corresponding polynuclear metal hydroxides intercalated between laminated Mont layers. Sn-Mont contains nanoparticles of polynuclear tin hydroxides which are surrounded by delaminated Mont layers. The formation mechanism for Sn-Mont previously proposed by us¹ can be applied to other metal ions-incorporated montmorillonites: When natural Na-Mont is dispersed in an aqueous M^{z+} solution to be arranged into a so-called card-house structure, the hydrated M^{z+} species are strongly pulled into the negative Mont layers and ion-exchanged, and then concentrated in the space between the layers (Figure 1). Washing the clay with water/methanol repeatedly and drying it promotes the hydrolysis and subsequent dehydration of the hydrated M^{z+} species leads to the precipitation of the corresponding metal hydroxides between the layers. Especially, in the case of Sn-Mont, Sn^{4+} species are incorporated in the amount far beyond the cation exchange capacity (CEC) of Mont, and finally form tin hydroxide nanoparticles, simultaneously causing the delamination of Mont layers.

In order to understand why Sn^{4+} species are specifically accumulated between the Mont layers, I deduced that the incorporation of the hydrated M^{z+} species between the Mont layers should be induced by the following two main

Table 1. The Mukaiyama aldol reaction of congested ketones **1** with silicon enolates **2** catalyzed by Sn-Mont.

			
Ketone 1	Silicon enolate 2	Time / h	Yield /% ^{a,b}
 1a		3	88 ^{c,d}
 1b		2	98
 1c		2	97
 1d	 2a	3	35
 1e		10	0
 1f		3	72
 1g		5	35 ^d
1a		1	96
1b	 2b	1.5	97
1c		1.5	99
1d		6	35
1e		7	96
1a		2	95 (62:38) ^e
1b	 2c	3	96 (43:57) ^e
1c		3	51
1d		7	58 (70:30) ^e
1e		8	79
1a		4	99 ^f
1b	 2d	5	76 ^{f,g}
1c		5	92 ^{f,h} (34 ^{a,f})
1d		10	0 ^f
1e		12	0 ^f
1a	 2e	3	96 ⁱ
1b		4	92 ⁱ

^a**1** (1.0mmol), **2** (2.0mmol), catalyst (40 mg), CH_2Cl_2 (2 mL), 0 °C. ^bDetermined by ¹H NMR. ^cSn-Mont was activated at 150 °C. ^d**1** (1.0mmol), **2** (1.1mmol), catalyst (20 mg). ^eThe molar ratio of threo and erythro diastereomers. ^fPerformed under reflux conditions. ^gDehydrated product **5bd** was also formed (23%). ^hCatalyst (100 mg). ⁱPerformed at RT.

interactions; (i) the interactions between M^{z+} and anionic Mont layers, and (ii) the interactions between M^{z+} and $M(OH)_x$. The interaction (i) can be evaluated by a free energy change in coordination ΔG_{coord} which is estimated from the hydrolysis equilibrium constants of M^{z+} species and the sorption data of metal species on Mont layers in the literatures. Meanwhile, the interaction (ii) is related to the precipitation ability of metal (hydr)oxides. Therefore, the interaction (ii) can be evaluated by a free energy change in oligomerization ΔG_{oligo} which is estimated from the dissolution equilibrium constants of metal (hydr)oxide crystals in water in the literatures. Judging from the order of ΔG_{coord} as $\text{Sn}^{4+} > \text{Ti}^{4+} > \text{Al}^{3+} > \text{Fe}^{3+}$ and the order of ΔG_{oligo} as $\text{Sn}^{4+} > \text{Ti}^{4+} > \text{Fe}^{3+} > \text{Al}^{3+}$, it is concluded that the aggregation between tin hydroxide in Sn-Mont is greatly promoted and the resulting polymerized nanoparticles are precipitated much more than the other metal hydroxides.

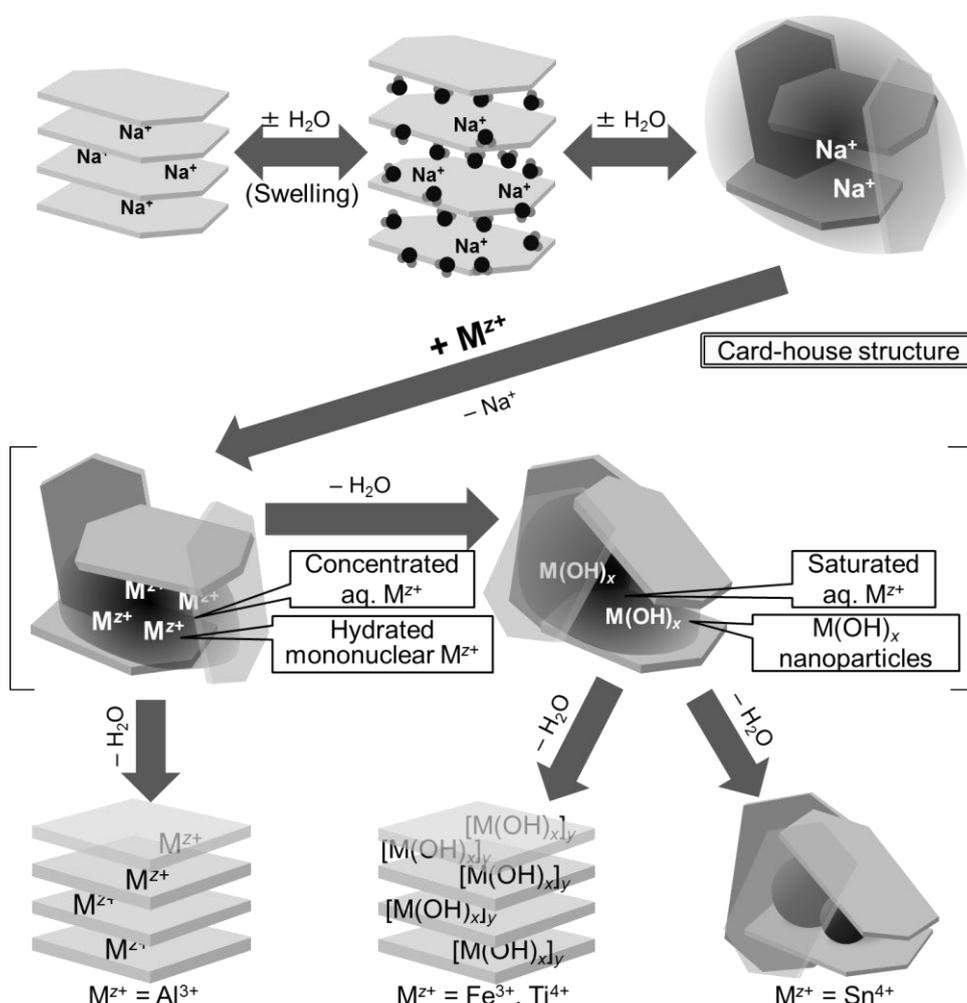


Figure 1. Supposed mechanism for the formation of M-Monts.

4. Development of titanium (hydr)oxide-embedded montmorillonite

In the incorporation process of hydrated M^{z+} species between Mont layers, as soon as the concentrated M^{z+} species precipitate to form metal hydroxide, further incorporation of M^{z+} species would happen until the precipitation stops. Therefore, it is reasonable to think that the lower the solubility of a metal hydroxide immediately becomes, the more easily the M^{z+} species precipitate. The solubility of the metal oxide or hydroxide phase initially decreases rapidly with increasing pH but levels off as hydrolysis in solution proceeds.² Therefore, an intentional increase in the pH of a solution can enrich M^{z+} species other than Sn^{4+} in the card-house structure of a clay, promoting more precipitation of the metal hydroxide as well as the delamination of Mont layers in a similar way to the synthesis of Sn-Mont. In order to develop a novel metal hydroxide-embedded

Table 2. The porosity and catalytic activity for the Mukaiyama aldol reaction of **1a** with **2a** of $\text{Ti}(\text{OH})_x$ -Mont.

Entry	Catalyst	Surface area /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Time /h	Yield /% ^{a,b}		
					3aa	4aa	5aa
1	Na-Mont	22	0.056	3	0	0	0
2	Sn-Mont	380	0.27	0.75	75	6	16
3	Ti(OH) _x -Mont	393	0.60	0.75	83	3	2
4	Ti-PILC	304	0.23	3	57	0	0
5	Ti-Mont	126	0.13	3	25	0	0
6	Bulk Ti(OH) ₄	302	0.22	3	0	0	0
7	Ti(OH) _x -Mont ^c	380	0.59	3	34	0	0
8	Ti(OH) _x -Mont ^d	172	0.53	3	0	0	0
9	TiO _x -Mont	361	0.55	1.25	91	0	0
10	Sn-Mont ^e	380	0.31	3	4	0	0

^a**1a** (1.0mmol), **2a** (1.1mmol), catalyst (20 mg), CH₂Cl₂ (2 mL), 0 °C. ^bDetermined by ¹H NMR. ^cNaOH (1 eq. to Ti⁴⁺) was added in the preparation. ^dNaOH (1.5 eq. to Ti⁴⁺) was added for the preparation. ^eThermally treated at 400 °C.

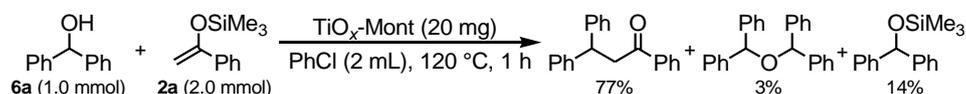
montmorillonite, I chose Ti(IV) of which solubility is the second-lowest after Sn(IV) at a high pH range in the M-Mont synthesis process.

For the preparation of a novel Ti-incorporated clay, aq. NaOH was added. To my delight, adding 0.75 eq. of NaOH to Ti^{4+} was of choice. ICP analysis revealed about 27 times as much amount of Ti as CEC was incorporated. The XRD pattern of the resulting clay showed no laminated structure but some peaks specific to titanium (hydr)oxide nanoparticles. N_2 sorption measurements proved that the clay had as high surface area as that of Sn-Mont, and its pore volume was much higher than conventional Ti-Mont and Ti-PILC as well as Sn-Mont (Table 2). Adding a more amount of NaOH did not improve the surface areas and pore volumes, probably because of the precipitation of titanium hydroxide outside the card-house structure of Mont layers. Hereafter, this novel Ti-incorporated clay material is called titanium hydroxide-embedded montmorillonite, $Ti(OH)_x$ -Mont. It is notable that $Ti(OH)_x$ -Mont was a definitively different porous material from Ti-PILC in point of delamination of Mont layers.

5. Solid acid catalysis of titanium (hydr)oxide-embedded montmorillonite for the Mukaiyama aldol reactions as well as the alkylation reactions of silicon enolates

The solid acid catalysis of $Ti(OH)_x$ -Mont was also evaluated by the Mukaiyama aldol reaction of acetophenone (**1a**) with its silicon enolate **2a** (Table 2). $Ti(OH)_x$ -Mont showed higher selectivity of silylated aldol product **3aa** than Sn-Mont under the same reaction conditions (entries 2 vs. 3). Note that $Ti(OH)_x$ -Mont was more reactive than Ti-PILC as well as Ti-Mont (entries 4 and 5). In addition, bulk $Ti(OH)_4$ scarcely exhibited the reactivity, indicating the assembly of $Ti(OH)_x$ with the Mont layer is crucial for gaining high acidity (entry 6). Interestingly, the catalytic activity drastically decreased when adding an equivalent or excess amount of NaOH to Ti^{4+} during the preparation of $Ti(OH)_x$ -Mont (entries 7 and 8). This is likely due to the neutralization of the positive charges of the titanium hydroxide surrounded by Mont layers. Moreover, the acidity of thermally-treated $Ti(OH)_x$ -Mont at 400 °C (TiO_x -Mont) was not deteriorated (entry 9), while Sn-Mont lost its acidity during the thermal treatment (entry 10).

Next, TiO_x -Mont-catalyzed direct alkylation of silicon enolate **2a** with benzhydrol (**6a**) was conducted (Scheme 1). The key of this reaction is the production of a carbocation intermediate through the dehydration of alcohol in the clay catalyst. Under the optimum reaction conditions, a desired alkylation product was obtained in good yield.



Scheme 1. The alkylation reaction of **2a** with **6a**.

6. Summary

I elucidated that Sn-Mont catalyzed the Mukaiyama aldol reactions with bulky ketones and that the strong interaction of Sn^{4+} with aluminosilicate layers of Mont as well as mutual interactions between $Sn(OH)_x$ were responsible for the delaminated, metal hydroxide-embedded structure of Sn-Mont. Furthermore, based on the formation mechanism of M-Mont, the novel titanium (hydr)oxide-embedded montmorillonite was developed. Especially, the high acid catalysis of $Ti(OH)_x$ -Mont thermally treated at 400 °C should be noted for the Mukaiyama aldol reactions of silicon enolates with bulky ketones. I was also successful in the direct alkylations of silicon enolates with alcohols catalyzed by $Ti(OH)_x$ -Mont.

References

1. Y. Masui, J. Wang, K. Teramura, T. Kogure, T. Tanaka, M. Onaka, *Micropor. Mesopor. Mater.* **2014**, *198*, 129–138, and references therein.
2. C. F. Baes, Jr., R. E. Mesmer, *Am. J. Sci.*, **1981**, *281*, 935–962.