

This article was downloaded by: [University of Haifa Library]

On: 20 August 2012, At: 10:54

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954

Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

Metal-cluster Ion Intercalated Clay and Stage n-like Structure

Kazuo Urabe^a, Hiromitsu Nagayasu^a & Yusuke Izumi^a

^a Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-01, Japan

Version of record first published: 04 Oct 2006

To cite this article: Kazuo Urabe, Hiromitsu Nagayasu & Yusuke Izumi (1998): Metal-cluster Ion Intercalated Clay and Stage n-like Structure, *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 311:1, 309-314

To link to this article: <http://dx.doi.org/10.1080/10587259808042403>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.tandfonline.com/page/terms-and-conditions>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan,

sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Metal-cluster Ion Intercalated Clay and Stage *n*-like Structure

KAZUO URABE, HIROMITSU NAGAYASU, and YUSUKE IZUMI
Department of Molecular Design and Engineering, Graduate School of
Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-01,
Japan

Various metal-cluster ion intercalated clays with first stage- and second stage-like structures were successfully synthesized and their physicochemical properties were examined briefly.

Keywords: metal-cluster ion; pillared clay; stage *n*-like structure; fluor-mica; rectorite; catalytic property

INTRODUCTION

Microporous pillared clay is an intercalation compound in which 'Al₁₃' oxide pillars as guest cations intercalate between every anionic layers of host clay. However, the applicability of pillared clay as a catalytic material has been restricted due to its scant cation-exchange capacity unlike zeolite, so that a catalytically-active transition metal cannot be incorporated into pillared clay. A solution to this problem was provided by American ceramists^[1] who employed the chemical reduction of interlayer copper ions in Cu²⁺-exchanged montmorillonite by ethyleneglycol. This material is regarded as metal-cluster ion pillared clay. On the other hand, we found that the interlayer cations, such as La³⁺ and Li⁺, are peculiarly and

irreversibly fixed by heating onto the cation-exchange sites in a swellable fluor-mica as host clay and the type of cations control the structures of pillared FM by 'Al₁₃' ions either first stage- or second stage-like^[2]. Here we report a successful attempt to synthesize various metal-cluster ion pillared clays with stage 1- and stage 2-like structures as shown in Fig. 1 and their physicochemical properties.

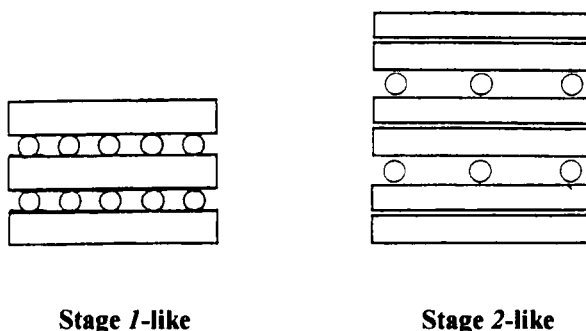


FIGURE 1 Stage 1- and stage 2-like structured metal-cluster pillared clays.

EXPERIMENTAL

The clay samples employed here are as follows; montmorillonite [$\text{Na}_{1/3}(\text{Al}_{2-1/3}\text{Mg}_{1/3})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$] (Kunipia F / Kunimine Ind.), hectorite [$\text{Na}_{1/3}(\text{Mg}_{3-1/3}\text{Li}_{1/3})(\text{Si}_4)\text{O}_{10}(\text{OH})_2$] (DPI-AW / American Colloid Co.), saponite [$\text{Na}_{1/3}(\text{Mg}_3)(\text{Si}_{4-1/3}\text{Al}_{1/3})\text{O}_{10}(\text{OH})_2$] (Benesa, Spain), fluor-mica^[2] [$\text{Na}(\text{Mg}_{2.68})(\text{Si}_4)\text{O}_{10}\text{F}_2$] (ME / CO-OP Chemical Co.), rectorite^[3] (Ohtoge, Japan). The Li⁺-fixed fluor-mica was prepared as described in the previous paper^[2].

Various metal-cluster ion pillared clay were prepared as follows. First, various metal ion-exchanged clays were prepared from the starting Na⁺ form clay using each metal ion aqueous solution by the common cation exchange

method at room temperature. Then, the dried metal ion-exchanged clay was dispersed in ethyleneglycol as a reducing agent and stirred as increasing the temperature. The formation of cluster-ion was visually observed by the color change of dispersed solution during the temperature range of 150-200 °C. The product was separated by centrifugation, washed three times with methanol and air-dried overnight at 60 °C.

X-ray diffraction (XRD) analysis was carried out employing an oriented clay film spread on a glass slide. The nitrogen adsorption on the sample was measured at -195 °C in order to examine its porous nature.

RESULTS AND DISCUSSION

Heating Cu^{2+} -exchanged montmorillonite (Cu^{2+} -M) in ethyleneglycol at about 200 °C causes the reduction of interlayer Cu^{2+} ions, accompanied with the change of solution color from blue to red. Fig. 2 illustrates the XRD spectra of Cu^{2+} -M and Cu^0 -cluster ion pillared one (Cu^0 -PM). Comparing (a) - (b) with (c) - (d) in Fig. 2, it seems that the calcination at 200 °C for 1 h brings about a collapse of interlayer space for Cu^{2+} -M, but not for Cu^0 -PM. This indicates that the Cu^0 -cluster ions with size of 5-6 Å are not only formed but also stably kept within montmorillonite interlayer space even at high temperature of 200 °C. The pillaring by Cu^0 -cluster ions brings about a marked increase in surface area from 20 m^2/g for Cu^{2+} -M to 172 m^2/g for Cu^0 -PM. The isotherm for N_2 gas adsorption over Cu^0 -PM fits a Langmuir-type well, indicating its microporous nature. By employing original clays other than montmorillonite, or hectorite, saponite and swellable fluor-mica, the Cu^0 -cluster ion pillared clays were also synthesized. Every pillared clay has a

similar basal spacing (d_{001}) of 15.2-15.6 Å, demonstrating a formation of 'first stage-like' structure in which Cu^0 -cluster ions with a similar size (5.6-6.0 Å) intercalate into every clay layers (thickness of 9.6 Å). Various metal cluster pillared montmorillonites were also obtained by using several metal ions except for Cu^{2+} . The easiness of reduction depends on the type of cations as follows; $\text{Ni,Cu,Ru}(200^\circ\text{C}) < \text{Rh}(175) < \text{Ir, Pt}(160) < \text{Pd, Au}(140)$. The value in each parenthesis means the temperature where the color change by reduction begins. This order fairly correlates with the standard oxidation-reduction potential of metal ions. The pillared one (Pd, Au) produced at lower temperature has smaller interlayer distance (I.D.; 3-4 Å) and lower specific surface area (S.A.; 20-30 m^2/g), while the pillared one (Ni,Cu,Ru) formed at relatively higher temperature has larger I.D. (5-6 Å) and higher S.A. (about 100 m^2/g).

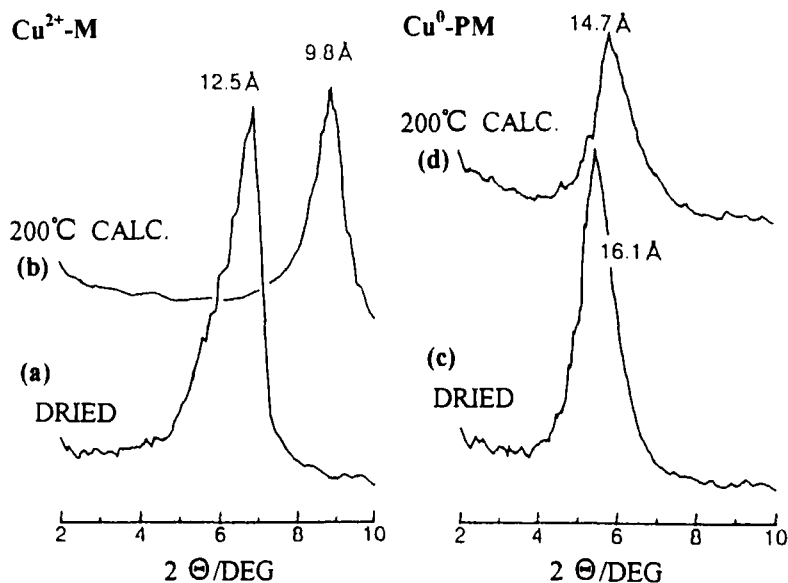


FIGURE 2 XRD spectra of $\text{Cu}^{2+}\text{-M}$ (a,b) and $\text{Cu}^0\text{-PM}$ (c,d).

In order to synthesize 'second stage-like' structured pillared clays, a rectorite and Li^+ -fixed FM were adopted as starting clays. Rectorite^[3] belongs to the class of regularly interstratified clay, or a natural one having a stage 2-like structure. Li^+ -fixed FM (Li^+ -FM) has been recently found by ourselves^[2] to form a stage 2-like structured pillared clay by ' Al_{13} ' ions. Fig. 3 illustrates XRD spectra of Cu^0 -cluster pillared rectorite (Cu^0 -PR) and Ni^0 -cluster pillared Li^+ -FM (Ni^0 -P(Li^+ -FM)) together with a stage 1-like structured Cu^0 -cluster pillared FM (Cu^0 -PFM) without Li^+ fixation treatment. The XRD peaks of Cu^0 -PR show $d_{001}=25.2$ and $d_{002}=12.3$ Å, indicating a formation of stage 2-like structure where Cu^0 clusters with size of 6 Å are held regularly between two clay layers (thickness of 19.2 Å). For Ni^0 -P(Li^+ -FM), a stage 2-like structure was also formed as well as a stage 1-like structure that was only formed in Cu^0 -PFM.

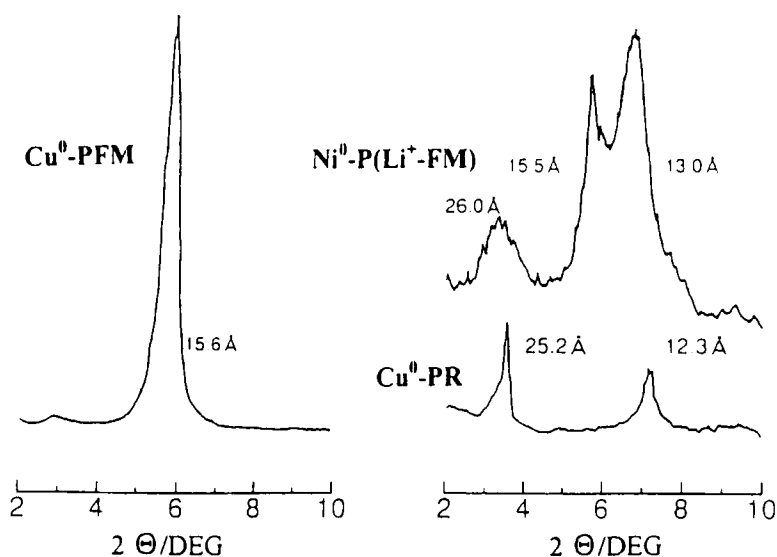


FIGURE 3 XRD spectra of Cu^0 -PR, Ni^0 -P(Li^+ -FM) and Cu^0 -PFM.

The thermal stability of metal cluster intercalated into interlayer space seems to be dominated by the type of host clay, especially the difference of isomorphous substitution. The pillared derivatives from *tetrahedrally* substituted clay, or saponite and rectorite^[3], are much more heat-stable than those from octahedrally substituted one, hectorite and fluor-mica. Interestingly, the XRD spectrum of Cu⁰-PR hardly changes by heating up to 500 °C. Thus, the Ni-cluster ion intercalated saponite and rectorite work as efficient catalysts for the selective ether formation reaction from *n*-butyl alcohol.

In summary, the first stage-like structured metal-cluster pillared clays are obtained by ethyleneglycol reduction of metal ion-exchanged *smectites* and the easiness of reduction depends on the type of metal ion. On the other hand, the second stage-like structured ones are synthesized using a regularly interstratified *rectorite* and *Li*⁺-fixed FM as starting clays.

Acknowledgments

The authors thank Dr. H. Tateyama (Kyushu National Industrial Research Institute) and Prof. K. Kitajima (Shinshu Univ.) for stimulating discussions, and the Daikou Foundation for financial support of this work.

References

- [1.] P.B. Malla, P. Ravindranathan, S. Komarneni and R. Roy, *Nature*, **351**, 13 June, 555 (1991).
- [2.] K. Urabe, I. Kenmoku and Y. Izumi, in *Proc. 8th Inter. Symp. on Intercalation Compounds*, edited by J.E. Fischer, R.F. Frindt and S.A. Solin (Vancouver, 1995); *J. Phys. Chem. Solids*, **57**, (No.6-8) 1037 (1996).
- [3.] K. Urabe, N. Kouno, H. Sakurai and Y. Izumi, *Adv. Mater.*, **3**, 558 (1991).