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Communication

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Ionic Crystals $[M_3O(OOCC_6H_5)_6(H_2O)_3]_4[\alpha\text{-}SiW_{12}O_{40}]$ (M = Cr, Fe) as Heterogeneous Catalysts for Pinacol Rearrangement

Sayaka Uchida, Aldes Lesbani, Yoshiyuki Ogasawara, and Noritaka Mizuno*

School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku 113-8656, Tokyo

Ⓢ *Supporting Information*

ABSTRACT: Complexation of trinuclear oxo-centered carboxylates with a silicododecatungstate resulted in the formation of ionic crystals of $[M_3O(OOCC_6H_5)_6(H_2O)_3]_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O\cdot mCH_3COCH_3$ [M = Cr (**Ia**), Fe (**IIa**)]. Treatments of **Ia** and **IIa** at 373 K in vacuo formed guest-free phases **Ib** and **IIb**, respectively. Compounds **Ib** and **IIb** heterogeneously catalyzed the pinacol rearrangement to pinacolone with high conversion at 373 K, and the catalysis is suggested to proceed size selectively in the solid bulk.

The arrangement of molecular building blocks into ordered structures is a key topic in material chemistry. Especially, the design and synthesis of materials with nanosized spaces have extensively been investigated because of unique guest sorption, separation, and catalytic properties.[1] Classical examples are microporous zeolites composed of covalently bonded $[TO_4]$ (T = Si, Al) units.[1a] Recently, metal–organic frameworks or porous coordination polymers constructed with coordination bonds between metal ions and organic units have attracted attention because of characteristic features including well-ordered micropores, flexible and dynamic behaviors in guest sorption, and designable channel surface functionalities.[1b,c]

Ionic crystals composed of molecular ions (macroions) possess molecular-sized spaces and strong electric fields at the internal surface suitable for accommodating polar molecules. Therefore, ionic crystals have been studied as host materials for guest sorption and separation.[2] Previously, we have reported a series of ionic crystals exhibiting sorptive separation of water and small polar organic molecules.[2a,b] However, little is known of the heterogeneous catalysis within lattices of ionic crystals. Trinuclear oxo-centered carboxylate complexes $[M_3O(OOCR)_6(L)_3]^+$ (M = Cr, Mn, Fe, Ru, etc.; R = H, CH_3, C_2H_5, C_6H_5, etc.; L = H_2O, pyridine, etc.) have been widely studied for unique magnetic, electronic, and catalytic properties.[3] These macrocations can be used as building blocks to construct functional ionic crystals.[2a−c] In this Communication, complexation of macrocations $[M_3O(OOCC_6H_5)_6(H_2O)_3]^+$ (M = Cr, Fe) with $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$, which is a nanosized metal–oxide macroanion, was attempted to construct ionic crystals with unique catalytic properties.

Ionic crystals of $[Cr_3O(OOCC_6H_5)_6(H_2O)_3]_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O\cdot mCH_3COCH_3$ (**Ia**) and $[Fe_3O(OOCC_6H_5)_6(H_2O)_3]_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O\cdot mCH_3COCH_3$ (**IIa**) were crystallized from an acetone/water solution.[4] Fourier transform IR spectra of **Ia** and **IIa** showed characteristic bands of the constituent macroions, indicating maintenance of the molecular structures in the ionic crystals. Elemental analyses of **Ia** and **IIa** showed macrocation/macroanion ratios of 4:1. Single-crystal X-ray structure analyses of **Ia** and **IIa** showed that the crystallographic parameters were similar to each other.[5] The crystal structure of **Ia** is shown in Figure 1.

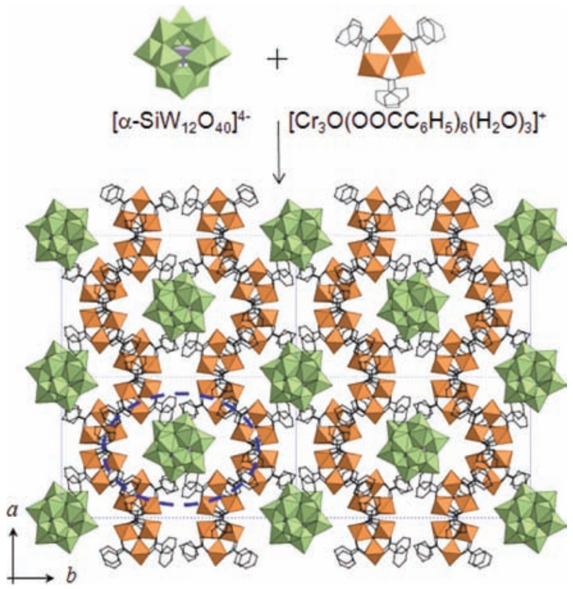

Figure 1. Crystal structure of **Ia**. Light green, purple, and orange polyhedra show the $[WO_6]$, $[SiO_4]$, and $[CrO_6]$ units, respectively. Blue broken oval show the eight-membered ring.

The macrocations formed an eight-membered ring (blue broken oval in Figure 1), and macroanions existed inside the rings. The distances between the benzoic groups of adjacent macrocations along the *a* and *c* axes were 3.6–3.9 Å, showing π–π interaction. The closest distance between the macrocations (oxygen atoms of the terminal water ligand) and macroanions (terminal oxygen atoms) was 3.6 Å, suggesting that oppositely charged macroions are assembled mainly by electrostatic interaction. Compound **Ia** possessed ca. 44% of the void volume (3.3×10^3 Å^3 per formula) filled with acetone and water of crystallization. Treatments of **Ia** and **IIa** at 373 K in vacuo for >3 h formed the corresponding guest-free phases

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$[M_3O(OOCC_6H_5)_6(H_2O)_3]_4[\alpha\text{-}SiW_{12}O_{40}]$ [M = Cr (**Ib**), Fe (**IIb**)].

Powder X-ray diffraction (XRD) patterns are shown in Figure 2. The powder XRD pattern of **Ia** (Figure 2b) fairly agreed with that calculated with the crystallographic data of **Ia** (Figure 2a). On the other hand, the powder XRD pattern of **Ib** (Figure 2c) showed broad signals, indicating that structure transformation occurs with the guest desorption. The broad signals could be reproduced with closer packing of the macroions in a unit cell of ca. 80% volume and a crystallite size of 15 nm (Figure 2c).[6] The broad signals were restored by exposure of **Ib** to an acetone/water vapor (Figure 2d), showing a reversible structure transformation. Similar structure transformations were also observed for **IIa** and **IIb**.

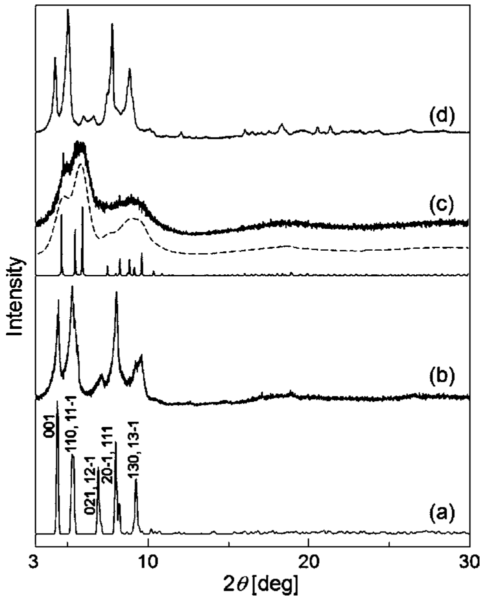

Figure 2. Powder XRD patterns. (a) Calculated with the crystallographic data of **Ia** and the experimental data of (b) **Ia**, (c) **Ib**, and (d) **Ib** under an acetone/water vapor. Broken and solid lines under part c show the calculated data with crystallite sizes of 15 nm and 10 μm, respectively, with $a = 22.3$, $b = 30.4$, $c = 20.6$, and $\beta = 119$. Numbers in part a show the Miller indices.

Compound **Ib** catalyzed the pinacol rearrangement to pinacolone with high conversion in toluene at 373 K. The yield of pinacolone was 79% after 12 h (Table 1 and Figure S1 in the Supporting Information).[7] 2,3-Dimethyl-1,3-butadiene formed by simple dehydration was a byproduct, and the amount increased with an increase in the reaction temperature. The reaction was completely stopped by the removal of **Ib** (Figure S3 in the Supporting Information). The inductively coupled plasma atomic emission spectrometry analyses showed that no chromium and tungsten species were leached into the reaction solution. These results show that the observed catalysis is truly heterogeneous. The catalytic activity did not change upon the reuse of **Ib**: Yields of pinacolone for the first and second reuse runs were 76% and 76%, respectively. Notably, **Ib** showed no reactivity toward the rearrangement of larger benzopinacol, suggesting that the catalysis of **Ib** is size-selective. *This is the first report on the heterogeneous size-selective acid catalysis within lattices of ionic crystals.*

Table 1. Pinacol Rearrangement at 373 K

catalyst	time [h]	convn [%]	yield[a] [%]	CB[b] [%]
Ib	12	100	79	98
IIb	6	100	80	98
$K_4[\alpha\text{-}SiW_{12}O_{40}]$	20	0	0	99
$[Cr_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$	20	5	3	99
$[Fe_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$	20	6	3	99
blank	20	0	0	99

[a]Yield of pinacolone. [b]CB = carbon balance. Reaction conditions: toluene, 3 mL; catalyst, 0.018 mmol (0.072 mmol for $[M_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$ (M = Cr, Fe); pinacol, 0.4 mmol (47.5 mg); naphthalene (internal standard), 0.2 mmol.

The pinacol rearrangement is generally catalyzed by Brønsted acids.[8] In the course of the reaction, protonation of the hydroxyl group of pinacol occurs followed by the formation of a carbocation intermediate.[8,9] It is well-known that metal aqua ions $[M(H_2O)_6]^{n+}$ dissociate protons and act as Brønsted acids.[11] The incorporation of $[Fe(H_2O)_n]^{3+}$ in aluminophosphates,[12] mesoporous silica,[12] and montmorillonites[13] largely enhanced the catalytic activity. Thermogravimetric (TG) analyses of **Ia** and **IIa** showed that aqua ligands of Cr^{3+} and Fe^{3+} are essentially maintained after treatment at 373 K (Figure S4 in the Supporting Information).[14] Therefore, aqua ligands of macrocations are possible active sites. Compound **IIb** showed higher catalytic activity than **Ib**.[15] The pK_a values of $[Cr(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ are 4.2 and 2.2, respectively,[16] and the acidity of $[Fe(H_2O)_6]^{3+}$ is higher because of the higher electronegativity of Fe: Fe–O bonds are more covalent and stronger, and dissociation of protons proceeds more easily.[11] Because $K_4[\alpha\text{-}SiW_{12}O_{40}]$ and $[M_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$ (M = Cr, Fe) were not active under the same conditions (Table 1), the combination of macrocations with macroanions in **Ib** and **IIb** is probably crucial for catalysis. Compounds **Ib** and **IIb** heterogeneously catalyzed the pinacol rearrangement to pinacolone with high conversion at 373 K (Table S1 in the Supporting Information).

In summary, ionic crystals composed of large macroions $[M_3O(OOCC_6H_5)_6(H_2O)_3]^+$ (M = Cr, Fe) and $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ were synthesized. Structure transformation occurred with the guest sorption–desorption. The guest-free phases were active for the pinacol rearrangement, and the activity of the ionic crystal containing Fe^{3+} was higher than that of Cr^{3+}, in line with the Brønsted acidity of the corresponding metal aqua ions. These results pave a way for unique heterogeneous catalysis of ionic crystals.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, pinacol-to-pinacolone rearrangement over various catalysts and conditions (Table S1), time courses of pinacol rearrangement catalyzed by **Ib** or **IIb** (Figure S1), geometrical optimization of pinacol sorbed in **Ia** (Figure S2), time course of pinacol rearrangement catalyzed by **Ib** and the effect of catalyst removal (Figure S3), TG analyses of **Ia** and **IIa** (Figure S4), time courses of pinacol rearrangement catalyzed by **Ia** or **IIa** (Figure S5), and X-ray data of **Ia** and **IIa** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tmizuno@mail.ecc.u-tokyo.ac.jp.

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(4) $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 10H_2O$ (0.035 mmol) was dissolved into 10 mL of water, and $NaClO_4$ (0.15 mmol) was added. The solution was filtered after stirring for 5 min (solution A). $[Cr_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$ (0.05 mmol) was dissolved in 10 mL of acetone (solution B). Solution B was added to solution A, the synthetic solution was kept at room temperature for 1 day, and green crystals of **Ia** were obtained (yield 30%). Compound **IIa** was synthesized by using $[Fe_3O(OOCC_6H_5)_6(H_2O)_3](NO_3)$ in a similar manner. Compounds **Ia** and **IIa** could also be synthesized by using $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$ as a starting material. In order to avoid contamination of **Ia** and **IIa** by the acidic protons of $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$, $K_4[\alpha\text{-}SiW_{12}O_{40}]\cdot 10H_2O$ was used. The catalytic activities of **Ib** and **IIb** were unchanged by the use of $H_4[\alpha\text{-}SiW_{12}O_{40}]\cdot nH_2O$ as a starting material.

(5) Crystallographic data for **Ia**: monoclinic, $P2_1/a$, $a = 22.3110(2)$ Å, $b = 33.0752(5)$ Å, $c = 23.0088(3)$ Å, $\beta = 117.0630(8)°$, $Z = 2$, $V = 15120.0(3)$ Å^3, crystal size 0.10 × 0.10 × 0.05 mm^3, $T = 183.1$ K, 41 842 reflections collected, 827 parameters, R1 $[I > 2\sigma(I)] = 0.1043$, wR2 = 0.3298, GOF = 1.174. Crystallographic data for **IIa**: monoclinic, $P2_1/a$, $a = 22.4142(2)$ Å, $b = 33.2833(4)$ Å, $c = 22.9409(3)$ Å, $\beta = 116.7664(4)°$, $Z = 2$, $V = 15280.5(3)$ Å^3, crystal size 0.10 × 0.10 × 0.05 mm^3, $T = 183.1$ K, 41 533 reflections collected, 667 parameters, R1 $[I > 2\sigma(I)] = 0.1191$, wR2 = 0.3733, GOF = 1.194.

(6) Calculated lattice parameters of **Ib**: monoclinic, $P2_1/a$, $a = 22.3$ Å, $b = 30.4$ Å, $c = 20.6$ Å, $\beta = 119°$, $V = 12\,200$ Å^3.

(7) About 5.0 mol mol^{-1} (ca. 30%) of pinacol was detected in the solid phase at 20% conversion (after 2 h). Upon completion of the reaction, 3.5 mol mol^{-1} (ca. 20%) of pinacolone formed was detected in the solid phase. These results suggest that the reaction proceeds in the solid bulk. The molecular diameters of pinacol and pinacolone are both ca. 7 Å, and geometrical optimization of pinacol sorbed in **Ia** (Figure S2 in the Supporting Information) showed that pinacol can be accommodated into the crystal lattice of **Ia**. The pinacol molecule is composed of single bonds and possesses conformational flexibility. Ionic crystals are composed of isotropic ionic bonds, which are different from anisotropic covalent bonds and coordination bonds, and can easily transform their crystal structures to adapt to polar guest molecules.[2] The structural flexibility of pinacol molecules and ionic crystals probably contributes to catalysis within the crystal lattice.

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(14) About 8 and 11 out of 12 aqua ligands per formula were maintained after the treatment of **Ia** and **IIa**, respectively. Because the treatment and reaction were performed at 373 K, the aqua ligands of Cr^{3+} and Fe^{3+} were probably mostly maintained under the reaction conditions. Moreover, the pinacol rearrangement is a dehydration reaction, and water molecules that formed in the reaction would coordinate to the coordinatively unsaturated Cr^{3+} and Fe^{3+} sites. Therefore, protons that dissociated from the aqua ligands (i.e., Brønsted acids) are possible active sites.

(15) Compounds **Ia** and **IIa** also catalyzed the pinacol rearrangement to pinacolone with high yields of 76% and 79%, respectively, and these values were similar to those of **Ib** and **IIb**. However, longer times of ca. 12 h (**Ia**) and 24 h (**IIa**) were needed to complete the reaction (Figure S5 in the Supporting Information). This is probably because exchange between pinacol molecules and crystallization solvents (acetone and water) would take place within the crystal lattice before the reaction.

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