Preparation of inorganic–organic composites as acid–base catalysts using HCa$_2$Nb$_3$–$_x$Ta$_x$O$_{10}$ and quaternary onium salts

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Inorganic–organic composites have been prepared using Dion–Jacobson-type layered perovskite compounds as base catalysts. Dodecyldibutylphosphonium bromide (C$_{12}$TPBBr), dodecyltriphenylphosphonium bromide (C$_{12}$TPPBr) or dodecyltrimethylammonium chloride (C$_{12}$TMA) were used as the organic species of the inorganic–organic composite. It was suggested that C$_{12}$TBP$^+$, C$_{12}$TPP$^+$, or C$_{12}$TMA$^+$ were intercalated by ion-exchange with interlayer H$^+$ of HCa$_2$Nb$_3$O$_{10}$. The acid–base reaction was evaluated by consecutive deacetalization–Knoevenagel reactions. The product of the second-step reaction of the inorganic–organic composite catalysts was obtained, which suggested that the composites were acid–base bifunctional materials. For composites prepared using HCa$_2$Nb$_{3–x}$Ta$_x$O$_{10}$ ($x = 1$, 2, and 3) as inorganic species, the base catalytic activity decreased with decreasing fraction of organic species. Therefore, the hydrophobicity of the layered compounds affected the catalytic activity of the composite. Various catalysts should be prepared using reported layered perovskite-type compounds having various compositions.

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Environment-friendly catalysts are currently attracting attention in the fields of green and sustainable chemistry. The coexistence of multiple functions, such as acid and base catalytic properties, has been studied to guide the development of multistep cascade reactions that are advantageous for minimizing energy usage and chemical waste.$^{1,4}$ To impart base catalytic activity to inorganic compounds, grafting of basic organic functional groups is often used. For example, acidic montmorillonite,$^5$ zeolite,$^6$ or mesoporous materials grafted with alkylamines behave as solid base catalysts.$^{7,18}$ In addition, it has been reported that precursors to zeolite and mesoporous silica with quaternary ammonium cations act as solid base catalysts.$^{9,14}$ In these materials, it is thought that the base sites are located at the siloxy anion (Si=O$^-$) on the inorganic surface, near the quaternary ammonium cations. These results indicate that a base site is formed by the interaction between metal oxides and organic cations. Therefore, it is interesting to investigate the base catalytic activity for composites containing organic cations. As alkylphosphonium cations are known as organic cationic species similar to quaternary alkylammonium cations, we attempted to prepare composites consisting of quaternary alkylphosphonium cations and a layered compound, and evaluated their base catalytic activities. Furthermore, the addition of basic properties to solid acid materials should produce acid–base bifunctional materials. We would like to propose this approach as a prospective method for functionalization of cation-exchangeable layered compounds.

Dion–Jacobson-type layered perovskite compounds with the general formula A$^+$[A$_{n-1}$B$_n$O$_{3n+1}$] (A, A$^+$: alkali, alkali earth; B: Ti, Nb, Ta, or Fe) have been reported.$^{15,17}$ These compounds have attracted interest due to their compositional variability and diverse chemical properties. In particular, compounds with A$^+$ = H are known as solid Brønsted acids. In addition, inorganic–organic composites can be prepared by the intercalation of organic species.$^{18,20}$ We previously synthesized composites based on Dion–Jacobson-type HLaNb$_2$O$_7$ and HCa$_2$Nb$_3$O$_{10}$ compounds with the addition of alkyltrimethylammonium (C$_n$TMA) and alkylpyridinium (C$_n$Py) cations.$^{23}$ However, HCa$_2$Nb$_3$O$_{10}$-based composites with other quaternary cations have not yet been reported, and the basic prop-
erties of composites containing C₄TMA and C₄Py cations have not yet been adequately studied. Therefore, in this study, we prepared inorganic–organic composites using HCa₂Nb₃₋ₓTaₓO₁₀ (x = 0, 1, 2, 3) as the inorganic species and C₄TMA or alkylphosphonium ions as the organic species. As described above, we synthesized HCa₂Nb₃O₁₀–C₄TMA composites for n = 12 to 18. In this study, a quaternary onium ion with a dodecyl (C₁₂) group was selected. Results of composite including C₁₂-group onium cation would be useful to evaluate various properties of composites including C₁₂–C₁₈-group onium cations. Base site formation by the interaction between a metal oxide and a quaternary onium cation was reported only for composites including quaternary ammonium cations. In order to investigate the effect of the cationic functional group, quaternary phosphonium-containing composites were prepared using dodecyltributyl and dodecyltriphenyl phosphonium ions, which are stable and readily available as high-purity reagents. The catalytic behavior and acid–base properties of these composites were evaluated for Knoevenagel reaction and consecutive deacetalization–Knoevenagel reactions.

Layered-perovskite-type HCa₂Nb₃₋ₓTaₓO₁₀ (x = 0, 1, 2, 3) compounds were used as the inorganic species of the inorganic–organic composites, and were obtained by ion-exchange using KCa₂Nb₃O₁₀ or RbCa₂Nb₃₋ₓTaₓO₁₀ (x = 1, 2, 3) KₐCa₂Nb₃O₇(2₄) and RbCa₂Nb₃₋ₓTaₓO₁₀ (x = 1, 2, 3) were synthesized via solid-state reactions of K₂CO₃, Rb₂CO₃, La₂O₃, CaCO₃, Nb₂O₅, and Ta₂O₅. The molar ratio of the starting materials was alkali carbonate (K₂CO₃ or Rb₂CO₃):CaCO₃:Nb₂O₅:Ta₂O₅= 1.5:4:3 – x:x, and they were mixed in ethanol using a mortar and pestle. KCa₂Nb₃O₁₀ was obtained by heating the precursor mixture at 1523 K for 18 h in air, while the RbCa₂Nb₃₋ₓTaₓO₁₀ (x = 1, 2, 3) series of compounds were obtained by heating the corresponding precursors at 1023 K for 12 h, and then at 1423 K for further 36 h in air. The K- and Rb-type samples were dispersed in 6 mol/L HCl aqueous solution and stirred at 333–343 K for protonation by ion exchange. Dodecyltributylphosphonium bromide (C₁₂TBPBr; Tokyo Chemical Industry Co., Ltd.; 98.0%), dodecyltriphenylphosphonium bromide (C₁₂TPPBr; Wako Pure Chemical Industries, Ltd.; 97.0%), or dodecyltrimethylammonium chloride (C₁₂TMACl; Tokyo Chemical Industry Co., Ltd.; 97.0%) were used as the organic species of the composite.

Inorganic–organic composites were prepared using the following procedure.2₃ First, 0.30 g of HCa₂Nb₃₋ₙTaₙO₁₀ was dispersed in 108.2 mL of C₁₂TBPBr, C₁₂TPPBr, or C₁₂TMACl aqueous solution in 1:1 molar ratio. The suspension was stirred at 303 K for 1 h. The obtained precipitate was filtered and dried at 333 K. The prepared samples are henceforth referred to as HCa₂NbO₁₀–C₁₂TBP, HCa₂NbO₁₀–C₁₂TPP, and HCa₂NbO₁₀–C₁₂TMA. Phase identification of the prepared samples was performed by powder X-ray diffraction (XRD) using a Rigaku Ultima IV X-ray diffractometer (Cu-Kα radiation, 40 kV, 40 mA). The acid amount of the samples was measured by titration with an aqueous ammonium solution. The organic species content was calculated from the carbon content determined by CHN elemental analysis using an Exeter Analytical Inc. CE-440M element analyzer.

The acid–base reaction was carried out by liquid-phase consecutive deacetalization–Knoevenagel reactions (Scheme 1). Benzaldehyde dimethylacetal (BDMA; 1 mmol), H₂O (1 mmol), ethyl cyanoacetate (1 mmol), catalyst (30 mg), and acetonitrile solvent (2 mL) were added to a glass reactor, and stirred with a magnetic stirrer at 343 K for 3 h. The sole Knoevenagel reaction was carried out using the following procedure. Benzaldehyde (1 mmol), ethyl cyanoacetate (1 mmol), catalyst (50 mg), and dimethyl sulfoxide solvent (3 mL) were added to a glass reactor and stirred at 303 K. The reacted solutions were analyzed by high-performance liquid chromatography with ultraviolet and refractive index detectors.

Figure 1 shows the XRD patterns of the HCa₂NbO₁₀–C₁₂TBP, HCa₂NbO₁₀–C₁₂TPP, and HCa₂NbO₁₀–C₁₂TMA. The (001) peaks of HCa₂NbO₁₀–C₁₂TBP, HCa₂NbO₁₀–C₁₂TPP, and HCa₂NbO₁₀–C₁₂TMA were observed at lower angles than that of HCa₂NbO₁₀. These results indicated that expansion of the interlayer space occurred due to intercalation of C₁₂TBP, C₁₂TPP, or C₁₂TMA cations. The d-spacings determined from the (001) peaks of HCa₂NbO₁₀–C₁₂TBP, HCa₂NbO₁₀–C₁₂TPP, and HCa₂NbO₁₀–C₁₂TMA samples were 2.90, 2.98, and 3.02 nm, respectively. A previous study of the HCa₂NbO₁₀–C₁₂Py composite with the same alkyl chain reported a d-spacing of 3.1 nm, where the organic species formed a monolayer with tilting in the interlayer. The d-spacings of the C₁₂TBP-, C₁₂TPP-, and C₁₂TMA-composites were similar to that of the C₁₂Py-composite, suggesting monolayer arrangement of organic cations.

The acid amount of inorganic–organic composites and the results of acid–base reactions in the one-pot process are shown in Table 1. The acid amount of HCa₂NbO₁₀–C₁₂TMA was smaller than those of HCa₂NbO₁₀–C₁₂TBP and HCa₂NbO₁₀–C₁₂TPP. The CHN elemental analysis...
showed that the carbon contents of HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TBP, HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TPP, or HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TMA were 7.5, 10.7, and 10.2 mass %, while the contents of the organic species were 0.26, 0.30, and 0.57 mmol/g, respectively. Therefore, the C$_{12}$TMA content in HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TMA was larger than the C$_{12}$TBP and C$_{12}$TPP contents in HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TBP and HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TPP, respectively. These results indicated that H$^+$ in the interlayer of HCa$_2$Nb$_3$O$_{10}$ was exchanged by C$_{12}$TBP$^+$, C$_{12}$TPP$^+$, or C$_{12}$TMA$^+$. The results of the one-pot reaction (Table 1) show that BDMA conversions for the composite catalysts were 86–100%, indicating that the deacetalization-step was promoted. As shown in Scheme 1, this step was accelerated by the acid catalyst. The BDMA conversions of HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TBP and HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TPP were slightly higher than that of HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TMA. In addition, the acid amounts of HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TBP and HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TPP were larger than that of HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TMA. These results suggested that the BDMA conversion is affected by the acid amount. When HCa$_2$Nb$_3$O$_{10}$ was used as the catalyst under the same reaction conditions, the BDMA conversion was 100% and ethyl α-cyanoacinnamate was not clearly observed. Ethyl α-cyanoacinnamate was a product of the second-step Knoevenagel reaction for all catalysts, indicating that a base site was formed in addition to the acid site. These results suggest that the acid and base catalytic activities exhibited by the composites were a result of intercalation of C$_{12}$TBP, C$_{12}$TPP, or C$_{12}$TMA cations into the HCa$_2$Nb$_3$O$_{10}$ solid acid. The selectivity of ethyl α-cyanoacinnamate for HCa$_3$Nb$_2$O$_{10}$-C$_{12}$TBP and HCa$_3$Nb$_2$O$_{10}$-C$_{12}$TPP is higher than that for HCa$_3$Nb$_2$O$_{10}$-C$_{12}$TMA. On the other hand, the amounts of C$_{12}$TBP and C$_{12}$TPP are smaller than that of C$_{12}$TMA in the composites. These results suggest that the amount of effective base sites in the composites does not correspond to that of the organic cation. Previous reports by Kubota et al. on a porous material precursor including a quaternary ammonium cation$^{9,10}$ suggest that the base sites exist around the pore mouth of the precursor. As HCa$_2$Nb$_3$O$_{10}$-based composites have a layered structure, the amount of quaternary onium cations at the edge of the layer and their arrangement are considered to affect the base catalytic activity. Therefore, detailed investigations into the composition and structure of the composites are necessary to clarify the formation mechanism of the base sites.

The basic catalytic activity of the composite was confirmed by the sole Knoevenagel reaction. Figure 2 shows results of the Knoevenagel reaction between benzaldehyde and ethyl cyanoacetate. When HCa$_2$Nb$_3$O$_{10}$-C$_{12}$TBP, HCa$_3$Nb$_2$O$_{10}$-C$_{12}$TPP, or HCa$_3$Nb$_2$O$_{10}$-C$_{12}$TMA was used as the catalyst, the yields of ethyl α-cyanoacinnamate increased with increasing reaction time. However, the reaction did not progress when the solid acid HCa$_2$Nb$_3$O$_{10}$ was used. Additionally, when C$_{12}$TBPBr, C$_{12}$TPPBr, or C$_{12}$TMACl was used as the catalyst under the same reaction conditions, the yields of ethyl α-cyanoacinnamate at 1 h were less than 1.6%. These results indicate that the starting materials of the composites had no base catalytic activity. Therefore, it is considered that the base sites were formed by interaction between HCa$_2$Nb$_3$O$_{10}$ and quaternary onium ions, such as C$_{12}$TBP, C$_{12}$TPP, or C$_{12}$TMA cations. Various precursors of mesoporous silica and zeolite, including quaternary ammonium cations, have been reported as base catalysts.$^{9-14}$ In the precursors, the base site is thought to be Si-O$^-$ near the quaternary ammonium ion in the inorganic framework.$^9$ In this study, we
observed the formation of the base sites on Nb–O⁺ near the quaternary onium ions in the HCa₂Nb₃O₁₀-based composites. In order to investigate the effects of the C₁₂TMA, C₁₂TBP, and C₁₂TPP cations, the catalytic activity under the same conditions as those for the Knoevenagel reaction of the HCa₂Nb₃O₁₀-dodecylamine (C₁₂A) composite was investigated. HCa₂Nb₂O₁₀-C₁₂A was obtained by stirring HCa₂Nb₂O₁₀ and C₁₂A (Tokyo Chemical Industry Co., Ltd.; 97.0%) at 343 K in water. The yield of ethyl α-cyanocinnamate at 1 h was 19%, indicating that a composite containing C₁₂A showed lower base catalytic activity than did the C₁₂TMA-, C₁₂TBP-, and C₁₂TPP-composites. This difference was attributed to the strong interaction between –NH₂ and the acid sites of HCa₂Nb₂O₁₀ in the HCa₂Nb₂O₁₀-C₁₂A composite, which resulted in neutralization. On the other hand, it is considered that interaction between the layered perovskite and a quaternary onium cation is required for the formation of a base site. In the Knoevenagel reaction, it was presumed that Nb–O⁺ near the quaternary onium cations in the HCa₂Nb₃O₁₀-based composites deprotonated ethyl cyanoacetate and the reaction proceeded. We found no significant difference in the yield among the composites including C₁₂TMA, C₁₂TBP, and C₁₂TPP. As shown in Fig. 2, the yields of ethyl α-cyanocinnamate for the composite exceeded 50%. In addition, no reaction occurred when C₁₂TMA, C₁₂TBP, and C₁₂TPP were used in the absence of HCa₂Nb₂O₁₀. These results indicated that composite formation is necessary for base catalytic activity.

Figure 3 shows the XRD patterns of HCa₂Nb₃₋ₓTaₓO₁₀ (x = 1, 2, 3) and HCa₂Nb₃₋ₓTaₓO₁₀-C₁₂TMA (x = 1, 2, 3). A diffraction peak with a d-spacing of 2.98 nm was observed for HCa₂Ta₂O₁₀-C₁₂TMA, similar to that of HCa₂Nb₂O₁₀-C₁₂TMA (Fig. 1). However, for HCa₂NbTa₂O₁₀-C₁₂TMA, a weak peak of 3.02 nm and peaks of HCa₂NbTaO₁₀ were observed. The XRD pattern for HCa₂Ta₂O₁₀-C₁₂TMA was similar to that for HCa₂TaO₁₀, indicating that no intercalation of C₁₂TMA occurred. The carbon contents, C₁₂TMA content, and base catalytic activity of HCa₂Nb₃₋ₓTaₓO₁₀-C₁₂TMA (x = 0, 1, 2, 3) are shown in Table 2. The C₁₂TMA content in the composites decreased with increasing Ta content. This result is consistent with the absence of additional XRD peaks for the HCa₂Ta₃O₁₀-C₁₂TMA sample. The yields of ethyl α-cyanocinnamate after 3 h of the Knoevenagel reaction decreased with decreasing C₁₂TMA content in the catalysts. It has been previously reported that the HCa₂-Ta₂O₁₀ solid acids cannot be isolated in the hydrated form. This indicates that the hydrophobicity of the perovskite layer affects the intercalation of C₁₂TMA and the base catalytic activity.

To summarize, herein we prepared inorganic–organic composites using HCa₂Nb₂O₁₀, which is a Dion–Jacobson-type layered perovskite compound whose chemical properties depend on the composition. The inorganic–organic composites showed base catalytic activity. The quaternary ammonium or phosphonium ions interact with the layered compound to form base sites, which function without being disturbed by the acid sites, allowing the consecutive acid–base reaction to proceed. Moreover, the inorganic–organic composites were prepared using a layered compound in which Nb was substituted by Ta. It has been revealed that partially substituted inorganic–organic composites have base catalytic activity. We believe that the acid–base properties can be designed independently using the studied Dion–Jacobson-type perovskites, various compositions and chemical properties for which have been demonstrated. Further studies of the interactions with various organic species and/or organic species contents in inorganic–organic composites are expected in order to enhance their base catalytic activities.

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Table 2. CHN elemental analysis results, C₁₂TMA contents, and base catalytic activities of HCa₂Nb₃₋ₓTaₓO₁₀-C₁₂TMA (x = 0, 1, 2, 3)

| Catalyst | Carbon content (mass %) | C₁₂TMA content (mmol/g) | Yield of ethyl α-cyanocinnamate by Knoevenagel reaction (%) |
|----------|-------------------------|-------------------------|----------------------------------------------------------|
| x = 0    | 10.2                    | 0.57                    | 76                                                       |
| x = 1    | 5.45                    | 0.30                    | 49                                                       |
| x = 2    | 1.13                    | 0.063                   | 36                                                       |
| x = 3    | 0.25                    | 0.014                   | 0                                                        |

*3 h reaction time.
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