# Design of Layered Silicate by Grafting with Metal Acetylacetonate for High Activity and Chemoselectivity in Photooxidation of Cyclohexane

Nao Tsunoji,[†] Yusuke Ide,*[,‡] Yuya Yagenji,[†] Masahiro Sadakane,[†] and Tsuneji Sano*[,†]

[†]Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

[‡]World Premier International (WPI) Research Center, International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

Ⓢ *Supporting Information*
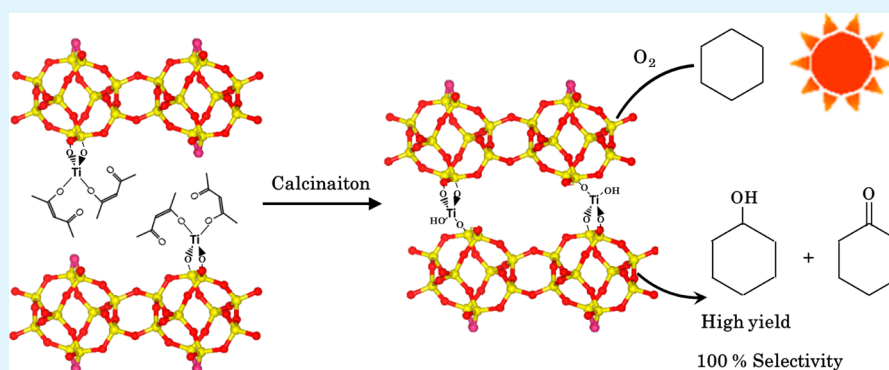
ABSTRACT: We succeeded in the immobilization of Ti(IV) acetylacetonate onto interlayer surfaces of a layered silicate HUS-2 (Hiroshima University Silicate-2, $Si_{20}O_{40}(OH)_4 \cdot 4[C_5H_{14}NO]$) and investigated the photocatalytic acitivity of Ti-incorporated HUS-2 toward the partial oxidation of cyclohexane to cyclohexanol and cyclohexanone under solar light irradiation. XRD, SEM/EDX, ^{13}C CP and ^{29}Si MAS NMR and UV−vis measurements of Ti-incorporated HUS-2 confirmed that the isolated tetrahedral Ti species were homogeneously immobilized onto silicate sheets via Si−O−Ti covalent bond and acetylacetonate ligands were removed after calcination. Ti-incorporated HUS-2 showed ca. 100% selectivity for partial cyclohexane oxidation and considerably higher yields (cyclohexanol and cyclohexanone) than TS-1, a typical Ti-containing zeolite. Higher yields were obtained when the calcined Ti-incorporated HUS-2 with a larger amount of the grafted Ti were used.

KEYWORDS: *layered silicate, grafting, titanium(IV)acetylacetonate, photocatalyst, cyclohexane,*

■ INTRODUCTION

Metallosilicate catalysts such as zeolites and mesoporous silicas with tetrahedrally coordinated transition metals species, especially Ti and V, covalently linked into silicate frameworks, have been utilized as oxidation catalysts for various reactions because of the specific property of the active sites.[1−3] They give specific and highly selective catalytic activities for epoxidation of alkenes and for oxidation of alkanes and alcohols by using oxidant or photoirradiation. The catalytic performances are quite different from those of bulk TiO_2 and V_2O_3, which consists of octahedrally coordinated species. Accordingly, the synthesis of more effective and active metallosilicate catalysts has been extensively investigated.[4−10] The amount of transition metal incorporated into the silicate framework, which directly affects the catalytic performances, can be controlled to some extent by changing the composition of starting materials.[4,6] When the amount of incorporated transition metal is greatly increased to improve their catalytic performances by conven-

tional methods, however, generation of unconvenient species such as metal and metal oxide are often observed because of the limitation of the amount of incorporated transition metals, which causes decrease in the activity and selectivity. To overcome such limitation of catalyst preparation, therefore, development of a novel route for design of catalysts with high activity and chemoselectivity by increasing density of active sites effectively is required.

Inorganic layered materials are attractive because of their large surface area derived from multistacking ultrathin layers having chemical and thermal stability and material diversity.[11] The grafting (covalent attachment) of functional units onto interlayer surfaces of layered materials is one of the most promising methods for design of the composite materials with
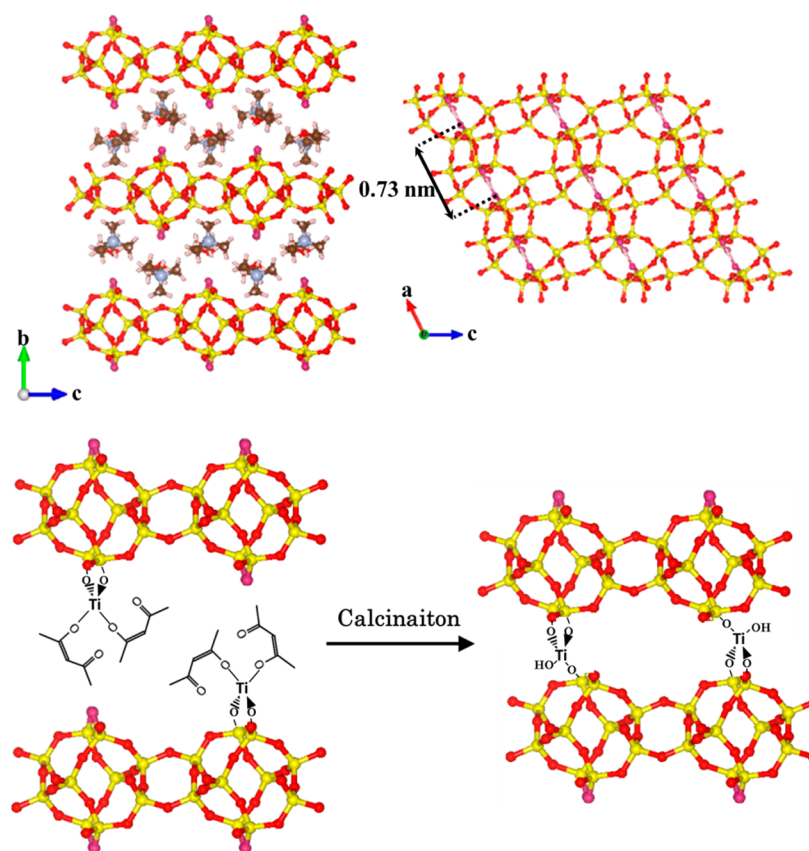
Figure 1. (top) Framework structure of HUS-2 and (bottom) scheme for grafting of Ti(acac)$_4$ onto interlayer surface of HUS-2.

hetero elements because of the regularity and numerousness of the connectable points between incorporated functional units and interlayer surfaces. Especially, the surface density of silanol groups of interlayer silicates, which can be regarded as connectable points, is higher than that of other materials such as zeolites and mesoporous silicas. The grafting was first reported by Rojo and Ruiz-Hitzky, who demonstrated the silylation of interlayer silanol group of a layered silicate with a silane coupling reagent.[12] Recently, in addition to silane coupling reagents,[13−20] alcohols,[21−23] phosphonic acids[24,25] and other hydroxyl-bearing organic molecules[26] have been successfully grafted onto the interlayer surfaces of various layered materials. Such grafting reactions allow control of the density and the interunit distance of the immobilized functional units in two-dimensional nanospaces at the angstrom level, which is important for the design of advanced materials such as single-site heterogeneous catalysts and photofunctional materials. Because the guest is irreversibly immobilized onto the interlayer surfaces, the resulting hybrid materials are sufficiently suitable for use in challenging practical applications. However, there are still few reports concerning the grafting of metal or metal oxide on the surfaces of layered materials,[27] which has the possibility to freely design advanced and innovative catalysts.

In this study, we report the grafting of titanium(IV) acetylacetonate as a representative metal acetylacetonate onto the interlayer surface of a layered silicate. We also show that the modified layered silicates with a controlled amount (density) of the grafted Ti are excellent photocatalysts for fine chemical synthesis under solar light irradiation when the acetylacetonate ligand is removed by calcination. Because a wide variety of metal acetylacetonates and various layered silicates with different framework topology are available, the present method may enable the design of diverse single-site heterogeneous catalysts.

■ EXPERIMENTAL SECTION

Preparation of Ti-Incorporated HUS-2. Layered silicate HUS-2[28] were synthesized by the hydrothermal treatment of starting gel, which had the chemical composition SiO$_2$:0.4 choline hydroxide:0.2 NaOH:5.5H$_2$O, at temperature 150 °C for 2 d. Hexhadecyltrimethylammonium (C$_{16}$TMA)-exchanged HUS-2 (C$_{16}$TMA-HUS) was prepared by the reaction of HUS-2 with an aqueous solution of hexadecyltrimethylammonium chloride. Ti-incorporated HUS-2 (x denotes grafted Ti residues per Si$_{20}$O$_{40}$(OH)$_4$ unit) was synthesized by the reaction of C$_{16}$TMA-HUS with Ti(acac)$_4$ followed by the removal of C$_{16}$TMA with washing. Ti(acac)$_4$ in isopropyl alcohol (ca. 63%, Wako) was used as received. C$_{16}$TMA-HUS (1.0 g) was mixed with the Ti(acac)$_4$ solution (5.38 mL of Ti(acac)$_4$) in ethanol/hexane (3:17 vol/vol; 100 mL) at room temperature for 3 d. After the evaporation of the solvent, the solid was washed twice with 0.1 M HCl/ethanol (1:1 vol/vol; 20 mL,), affording Ti$_{2.3}$-HUS. Ti$_{1.5}$-HUS and Ti$_{1.2}$-HUS were synthesized by a similar method except that C$_{16}$TMA-HUS was mixed with Ti(acac)$_4$ at 60 °C for Ti$_{1.5}$-HUS and room temperature in the presence of 2,2′-bipyridyl for Ti$_{1.2}$-HUS and the solids were separated by centrifugation, not by evaporation. For grafting of functional units onto silica surfaces, heterocyclic compounds such as pyridine and 2,2′-bipyridyl are often used to change the reactivity between interlayer silanol groups and gest species grafted. Therefore, we used the bipyridyl to control the amount of Ti incorporated.

Catalyst Tests. Photocatalytic oxidation reactions were carried out by photoirradiation with solar simulator (San-Ei Electric Co., Ltd.) in a closed stainless steel container equipped with a 75 mL of Pyrex glass vessel containing a mixture of catalyst (30 mg) and O$_2$-saturated solution of cyclohexane (2 mL) in acetonitrile (18 mL). The container was placed ca. 30 cm away from the light source to irradiate the

mixture by 1 solar (1000 Wm^{2-}) power light at 42 °C for 24 h with shaking. CO_2 and organic compounds were quantitatively analyzed by GC-FID and GC-TCD, respectively. Only cyclohexane, cyclohexanone, and cyclohexanol were detected in GC-FID.

RESULTS AND DISCUSSION

Metal acetylacetonates can be grafted onto oxide surfaces via ligand exchange with the surface hydroxy groups.[29,30] In this study, titanium(IV) acetylacetonate (Ti(acac)$_4$) was chosen as a typical metal acetylacetonate representative because Ti-containing porous silicas such as zeolite and mesoporous silica have been widely investigated as photocatalysts.[7−10] HUS-2 (Hiroshima University Silicate-2, $Si_{20}O_{40}(OH)_4 \cdot 4[C_5H_{14}NO]$), having interlayer choline cations and silanol groups (Figure 1),[28] was used as the layered silicate. Grafting of bulky organic molecules onto the interlayer surfaces of layered materials is usually accomplished by using the corresponding long-chain alkylammonium-exchanged forms as intermediates. Accordingly, the interlayer choline cations were first exchanged with hexadecyltrimethylammonium cations (C_{16}TMA) to afford C_{16}TMA-exchanged HUS-2 (C_{16}TMA-HUS), which then reacted with Ti(acac)$_4$, affording Ti$_x$-HUS.

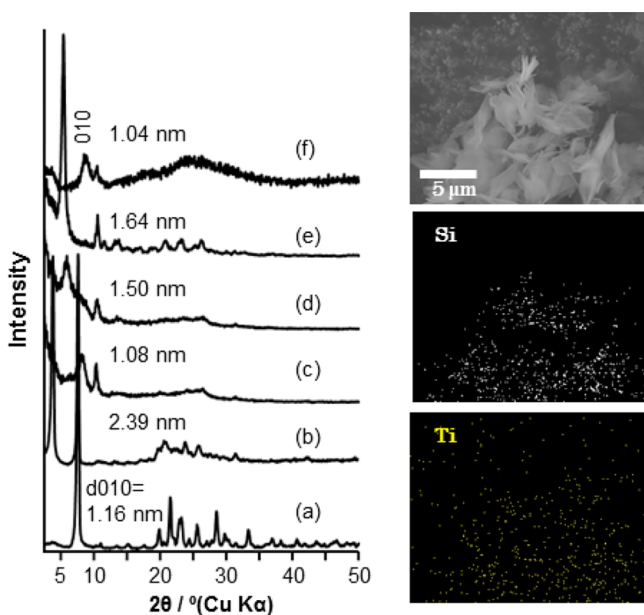Figure 2 (left) compares the X-ray diffraction (XRD) patterns of Ti$_x$-HUS to those of HUS-2 and C_{16}TMA-HUS.

Figure 2. (left) Powder X-ray diffraction patterns of (a) HUS-2, (b) C_{16}TMA-HUS, (c) Ti$_{1.2}$-HUS, (d) Ti$_{1.5}$-HUS, (e) Ti$_{2.3}$-HUS, and (f) calcined Ti$_{2.3}$-HUS. Insets show variation of basal spacing of Ti$_x$-HUS as a function of amount of grafted Ti(acac)$_4$. (right) FE-SEM image of Ti$_{2.3}$-HUS and corresponding elemental mapping (bottom).

In the XRD patterns of Ti$_x$-HUS, the peaks attributed to basal spacing diffraction and in-plane diffraction were observed around 5 and 10 degrees, respectively. The basal spacings of Ti$_x$-HUS differ from that of HUS-2 in a manner that dependent on the amount of the grafted Ti(acac)$_4$. The ^{29}Si MAS NMR spectra of Ti$_x$-HUS are also shown in Figure 3(left). The two resonance peaks between −90 and −100 ppm were assigned to the Q^3 structure, whereas the three resonance peaks between −105 and −120 ppm were assigned to the Q^4 structure, based on the ^{1}H−^{29}Si CP-MAS NMR measurements (see Figure S1 in the Supporting Information). The integral ratio of Q^3/Q^4
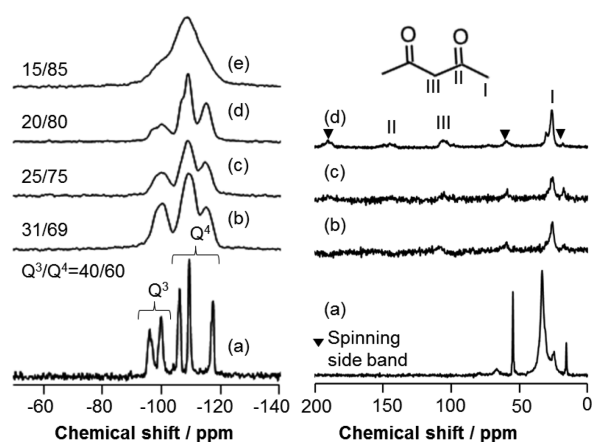

Figure 3. (left) ^{29}Si MAS NMR spectra of (a) C_{16}TMA-HUS, (b) Ti$_{1.2}$-HUS, (c) Ti$_{1.5}$-HUS, (d) Ti$_{2.3}$-HUS, and (e) calcined Ti$_{2.3}$-HUS. (right) ^{13}C CP-MAS NMR spectra of (a) C_{16}TMA-HUS, (b) Ti$_{1.2}$-HUS, (c) Ti$_{1.5}$-HUS, and (d) Ti$_{2.3}$-HUS.

signals, which reflects the amount of interlayer silanol groups, is substantially smaller for Ti$_x$-HUS relative to C_{16}TMA-HUS and decreases with increasing the amount of Ti(acac)$_4$ grafted. Furthermore, in the ^{13}C CP-MAS NMR spectra of Ti$_x$-HUS, signals from Ti(acac)$_4$ are observed whereas those from C_{16}TMA are not (Figure 3(right)). The above results indicate that Ti(acac)$_4$ was immobilized onto the silicate sheet via covalent Si−O−Ti bonds and C_{16}TMA barely remained in Ti$_x$-HUS. The compositions of the grafted Ti(acac)$_4$ for Ti$_{1.2}$-HUS, Ti$_{1.5}$-HUS, and Ti$_{2.3}$-HUS were calculated as Ti($C_5H_7O_2$)$_{1.4}$, Ti($C_5H_7O_2$)$_{1.8}$, and Ti($C_5H_7O_2$)$_{1.8}$, respectively, based on the amounts of Ti and acetylacetonate ligand (Table 1). Therefore, approximately half of the acetylacetonate ligands of Ti(acac)$_4$ in Ti$_x$-HUS remain. Judging from (1) the basal spacing (1.08−1.64 nm), (2) the long distance (0.73 nm) between the adjacent SiOH/SiO$^-$ pairs on the silicate sheet, indicating no possibility for formation of Ti−O−Ti covalent bond between the grafted Ti species, and (3) the convenient distance (0.25 nm) between two reactive functional groups (SiO$^-$/SiOH) for dipodal grafting of Ti(acac)$_4$, Ti(acac)$_4$ are grafted in a dipodal fashion with Ti−O−Si bridges, not but pillars the adjacent sheets, to leave two acetylacetonate ligands in Ti$_x$-HUS (Figure 1). As shown in Figure 2, the XRD patterns of Ti$_x$-HUS are indicative of a single phase (if the grafted Ti(acac)$_4$ are segregated, the basal spacing (010) peaks should split) and the basal spacings of Ti$_x$-HUS increase with increasing the amount of grafted Ti(acac)$_4$. Also, in the elemental mapping of Ti$_x$-HUS (Figure 2(right)), Ti was evenly distributed in the product. Similar results have been shown for the organic derivatives of layered materials with silane coupling reagents, in which the spatial distribution of the grafted silyl groups appears to be controlled.[14]

The remaining acetylacetonate ligand in Ti$_x$-HUS was removed by calcination at 400 °C for 6 h as evidenced by the ^{13}C CP-MAS NMR spectra, thermogravimetry-differential thermal analyses and CHN elemental analyses of Ti$_x$-HUS after calcination (see Figures S2 and S3 and Table S1 in the Supporting Information). Spectra a and b in Figure 4 show the UV−vis spectra of Ti$_{2.3}$-HUS before and after calcination, respectively. Upon calcination, the 320−450 nm absorption band from the $\pi-\pi^*$ transition in the acetylacetonate ligand[29] disappears and an absorption band appears at 220 nm. This band is often observed in Ti-incorporated zeolites such as TS-1

4618

dx.doi.org/10.1021/am500515p | ACS Appl. Mater. Interfaces 2014, 6, 4616−4621

Table 1. Compositions and Photocatalytic Performance of Ti$_x$-HUS before and after Calcination in the Selective Cyclohexane Oxidation under Simulated Solar Light

	acac/Ti[d]	Ti (wt %)	yield (μmol)[e]			[CHone+CHnol] selectivity (%)[f]
			CHone	CHol	CO$_2$	
Ti$_{1.2}$-HUS	1.4	4.0	3.4	4.1	n. d.	>99
Ti$_{1.2}$-HUS cal[a]		4.6	4.4	6.1	n. d.	>99
Ti$_{1.5}$-HUS	1.8	4.9	3.0	4.0	n. d.	>99
Ti$_{1.5}$-HUS cal[a]		5.6	6.1	6.7	n. d.	>99
Ti$_{2.3}$-HUS	1.8	6.5	4.9	7.5	n. d.	>99
Ti$_{2.3}$-HUS cal[a]		8.3	12.7	12.6	n. d.	>99
TS-1[b]		2.2	2.4	3.7	n. d.	>99
TiO$_2$ (P25)[c]			39.7	13.6	126.0	72

[a]Calcined at 400 °C under air flow. [b]A reference catalyst, ARC-TS1CL, Catalysis Society of Japan (Si/Ti molar ratio of 35). [c]Irradiation time, 6 h. [d]Molar ratio calculated from the amounts of Ti and acetylacetonate determined by the inductively coupled plasma atomic emission spectroscopy of the dissolved products and thermogravimetric-differential thermal analysis under air flow of the products, respectively. The mass loss from 250 to 500 °C was assumed because of the oxidative decomposition of acetylacetonate. [e]CHone and CHol are cyclohexannoe and cyclohexanol, respectively. [f][formed CHone] + [formed CHol]}/{[formed CHone] + [formed CHol] + 1/6[formed CO$_2$]} × 100.
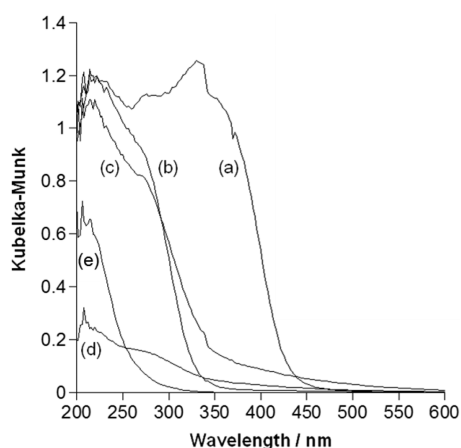
Figure 4. UV−vis spectra of (a) Ti$_{2.3}$-HUS, (b) calcined Ti$_{2.3}$-HUS, (c) calcined Ti$_{1.5}$-HUS, (d) calcined Ti$_{1.2}$-HUS, and (e) TS-1.

(Figure 4e) and is indicative of the presence of isolated tetrahedral Ti species. The absorbance at 220 nm increases with increasing the amount of grafted Ti(acac)$_4$. These results strongly suggest that the grafted Ti(acac)$_4$ is homogeneously distributed on the silicate sheet. Also, the basal spacing drastically decreases (Figure 2 f) and the integral ratio of Q^3/Q^4 signals for Ti$_{2.3}$-HUS slightly decreases upon calcination. As can be seen in Figure S4 in the Supporting Information, a peak assigned to Si−O−Ti bond was observed at ca. 960 cm^{-1} in FT-IR spectrum of Ti$_{2.3}$-HUS cal, indicating effective grafting of

Ti species onto interlayer surfaces of HUS-2. Furthermore, the N$_2$ adsorption isotherms of Ti$_{2.3}$-HUS before and after calcination showed that the amount of micropore-adsorbed N$_2$ increased upon calcination (see Figure S5 and Table S2 in the Supporting Information). All Ti$_x$-HUS cal showed basal spacings of ~1.0 nm, which were larger than that of HUS-2 calcined and dependent on the amount of the grafted Ti (see Figure S6 in the Supporting Information), indicating that upon the removal of the remaining acetylacetonate ligands, a part of the grafted Ti(acac)$_4$ links to the surface silanol group forming pillars that connect the adjacent silicate sheets (Figure 1). Because square-planar configuration for Ti is unlikely, one of the two remaining acetylacetonate ligands is likely to be converted to a hydroxy group (Figure 1). The shoulders observed in the 250−450 nm range in the UV−vis spectra of calcined Ti$_x$-HUS (Figure 4) likely indicate the presence of such Ti−OH species.[6] However, we could not rule out the possible presence of octahedral Ti species in the calcined Ti$_x$-HUS. Although TEM observation was carried out, we could not find out any Ti oxide particles in the TEM image as shown in Figure S7 in the Supporting Information. The oxidation state of Ti species incorporated in Ti$_x$-HUS was measured by XPS. The peak of Ti2p$_{3/2}$ attributed to Ti^{4+} (isolated tetrahedral Ti species) in the silicate framework was clearly observed at 460 eV of binding energy (see Figure S8 in the Supporting Information). However, the peak at 457.9 eV attributed to TiO$_2$ was hardly observed, indicating no formation of Ti oxide particles.

Zeolites and mesoporous silicas with isolated tetrahedral Ti are important single-site photocatalysis due to electron transfer from O^{2-} to Ti^{4+} ions upon excitation by UV irradiation, resulting in the formation of pairs of trapped hole (O$^-$) and electron (Ti^{3+}) centers.[10] We carried out the partial oxidation of cyclohexane to cyclohexanol (CHol) and cyclohexanone (CHone), one of the most important synthetic reactions in chemical industry, using Ti$_x$-HUS (before and after calcination) as photocatalysts under simulated solar light irradiation. TS-1, typical Ti-containing zeolite, and P25, a mixture of anatase and rutile type TiO$_2$, were used as references under the same irradiation conditions (Table 1). Although TiO$_2$ (P25) exhibited lower chemoselectivity because of the generation of a large amount of CO$_2$, TS-1 showed close to 100% chemoselectivity for partial oxidation. The completely oxidized product CO$_2$ barely formed. Our Ti$_x$-HUS also showed ~100% chemoselectivity. The yields of CHone and CHol were 3.4 and 4.1 μmol for Ti$_{1.2}$-HUS, 3.0 and 4.0 μmol for Ti$_{1.5}$-HUS, and 4.9 and 7.5 μmol for Ti$_{2.3}$-HUS. These values were higher than those for TS-1 (2.4 μmol of CHone and 3.7 μmol of CHol). When the reaction was carried out over the Ti$_{2.3}$-HUS under no irradiation condition, CHol, CHone and CO$_2$ were not formed. The considerable increase in the yields of CHone and CHol was observed when the calcined Ti$_x$-HUS was used. The yields of CHone and CHol were 4.4 and 6.1 μmol for Ti$_{1.2}$-HUS cal, 6.1 and 6.7 μmol for Ti$_{1.5}$-HUS, and 12.7and 12.6 μmol for Ti$_{2.3}$-HUS, respectively. Accordingly, both the interlayer pores created by removing of acetylacetonate ligands and pillaring of HUS-2 with Ti(acac)$_4$ and the isolated and tetrahedrally coordinated Ti grafted onto the silicate sheets played important roles in photocatalysis. Moreover, it was also found that the yields of CHone and CHol increased with the amount of incorporated Ti. These results strongly suggest that the larger amount of incorporated Ti yielded more effectively CHone and CHol because the isolated and tetrahedrally coordinated Ti

species was homogeneously distributed in the silicate surfaces and acted as a single active site. This conceptually new methodology can be used for the accurate construction of similar composite materials. Co-grafting of other metal acetylacetonates is now under investigation for further optimization of the photocatalytic performance.

CONCLUSIONS

We successfully grafted titanium(IV) acetylacetonate onto the interlayer surface of the layered silicate HUS-2. The Ti-incorporated (pillared) layered silicate showed a high photo-catalytic activity and excellent chemoselectivity in the partial cyclohexane oxidation to cyclohexanone and cyclohexanol under simulated solar light irradiation.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CHN elemental analysis results of Ti$_x$-HUS before and after calcination; ^{29}Si CP-MAS NMR spectra of Ti$_3$-HUS before and after calcination; ^{13}C CP-MAS NMR spectra of Ti$_x$-HUS after calcination; TG-DTA curves of Ti$_x$-HUS before and after calcination; FT-IR spectra of C$_{16}$TMA-HUS and Ti$_{2.3}$-HUS before and after calcination; N$_2$ adsorption isotherms and XRD patterns of calcined Ti$_x$-HUS and HUS-2; TEM image of Ti$_{2.3}$-HUS after calcination; and XPS spectrum of Ti$_{2.3}$-HUS after calcination. These materials are available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: tsano@hiroshima-u.ac.jp.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Centi, G.; Trifiro, F. *New Developments in Selective Oxidation*; Elsevier: Amsterdam, 1990.

(2) Arends, I. W. C. E.; Sheldon, R. A.; Wallau, M.; Schuchardt, U. Oxidative Transformations of Organic Compounds Mediated by Redox Molecular Sieves. *Angew. Chem., Int. Ed.* **1997**, *36*, 1144−1163.

(3) Notari, B. Titanium Silicate: A New Selective Oxidation Catalyst. *Stud. Surf. Sci. Catal.* **1991**, *60*, 343−352.

(4) Blasco, T.; Camblor, M. A.; Corma, A.; Esteve, P.; Guil, J. M.; Martinez, A.; Perdigón-Melón, J. A.; Valencia, S. Direct Synthesis and Characterization of Hydrophobic Aluminum-Free Ti−Beta Zeolite. *J. Phys. Chem. B* **1998**, *102*, 75−88.

(5) Xia, Q.-H.; Chen, X.; Tatsumi, T. Epoxidation of cyclic alkenes with hydrogen peroxide and tert-butyl hydroperoxide on Na-containing Ti zeolites. *J. Mol. Catal. A:Chem.* **2001**, *176*, 179−193.

(6) Fan, W.; Duan, R. G.; Yokoi, T.; Wu, P.; Kubota, Y.; Tatsumi, T. Synthesis, crystallization mechanism, and catalytic properties of titanium-rich TS-1 free of extraframework titanium species. *J. Am. Chem. Soc.* **2008**, *130*, 10150−10164.

(7) Corma, A.; Garcia, H. Zeolite-based photocatalysts. *Chem. Commun.* **2004**, 1443−1459.

(8) Shiraishi, Y.; Saito, N.; Hirai, T. Titanosilicate Molecular Sieve for Size-Screening Photocatalytic Conversion. *J. Am. Chem. Soc.* **2005**, *127*, 8304−8306.

(9) Rodrigues, S.; Ranjit, K. T.; Uma, S.; Martyanov, I. N.; Klabunde, K. Single-Step Synthesis of a Highly Active Visible-Light Photocatalyst for Oxidation of a Common Indoor Air Pollutant: Acetaldehyde. *J. Adv. Mater.* **2005**, *17*, 2463−2467.

(10) Mori, K.; Yamashita, H.; Anpo, M. Photocatalytic reduction of CO$_2$ with H$_2$O on various titanium oxide photocatalysts. *RSC Adv.* **2012**, *2*, 3165−3172.

(11) Okada, T.; Ide, Y.; Ogawa, M. Organic−Inorganic Hybrids Based on Ultrathin Oxide Layers: Designed Nanostructures for Molecular Recognition. *Chem. Asian J.* **2012**, *7*, 1980−1992.

(12) Ruiz-Hitzky, E.; Rojo, J. M. Intracrystalline grafting on layer silicic acids. *Nature* **1980**, *287*, 28−30.

(13) Takahashi, N.; Kuroda, K. Materials design of layered silicates through covalent modification of interlayer surfaces. *J. Mater. Chem.* **2011**, *21*, 14336−14353.

(14) Ogawa, M.; Okutomo, S.; Kuroda, K. Control of Interlayer Microstructures of a Layered Silicate by Surface Modification with Organochlorosilanes. *J. Am. Chem. Soc.* **1998**, *120*, 7361−7362.

(15) Ide, Y.; Ogawa, M. Surface modification of a layered alkali titanate with organosilanes. *Chem. Commun.* **2003**, *11*, 1262−1263.

(16) Ide, Y.; Ogawa, M. Interlayer modification of a layered titanate with two kinds of organic functional units for molecular specific adsorption. *Angew. Chem., Int. Ed.* **2007**, *46*, 8449−8451.

(17) Ide, Y.; Torii, M.; Tsunoji, N.; Sadakane, M.; Sano, T. Molecular recognitive adsorption of aqueous tetramethylammonium on the organic derivative of Hiroshima University Silicate-1 with a silane coupling reagent. *Chem. Commun.* **2012**, *48*, 7073−7075.

(18) Osterloh, F. E. Solution Self-Assembly of Magnetic Light Modulators from Exfoliated Perovskite and Magnetite Nanoparticles. *J. Am. Chem. Soc.* **2002**, *124*, 6248−6249.

(19) Ruiz, V. S. O.; Petrucelli, G. C.; Airoldi, C. Inorganic−organic hybrids derived from lamellar acidic kenyaite immobilizations for cation removal at the solid/liquid interface. *J. Mater. Chem.* **2006**, *16*, 2338−2346.

(20) Matsuo, Y.; Tabata, T.; Fukunaga, T.; Fukutsuka, T.; Sugie, Y. Preparation and characterization of silylated graphite oxide. *Carbon* **2005**, *43*, 2875−2882.

(21) Tunney, J. J.; Detellier, C. Interlamellar covalent grafting of organic units on kaolinite. *Chem. Mater.* **1993**, *5*, 747−748.

(22) Mitamura, Y.; Komori, Y.; Hayashi, S.; Sugahara, Y.; Kuroda, K. Interlamellar esterification of H-magadiite with aliphatic alcohols. *Chem. Mater.* **2001**, *13*, 3747−3753.

(23) Takahashi, S.; Nakato, T.; Hayashi, S.; Sugahara, Y.; Kuroda, K. Formation of Methoxy-Modified Interlayer Surface via the Reaction between Methanol and Layered Perovskite HLaNb$_2$O$_7$·xH$_2$O. *Inorg. Chem.* **1995**, *34*, 5065−5069.

(24) Guimarães, J. L.; Peralta-Zamora, P.; Wypych, F. Covalent Grafting of Phenylphosphonate Groups onto the Interlamellar Aluminol Surface of Kaolinite. *J. Colloid Interface Sci.* **1998**, *206*, 281−290.

(25) Shimada, A.; Yoneyama, Y.; Tahara, S.; Mutin, P. H.; Sugahara, Y. Interlayer surface modification of the protonated ion-exchangeable layered perovskite HLaNb$_2$O$_7$·xH$_2$O with organophosphonic acids. *Chem. Mater.* **2009**, *21*, 4155−4162.

(26) Wang, C.; Tang, K.; Wang, D.; Liu, Z.; Wang, L.; Zhu, Y.; Qian, Y. A new carbon intercalated compound of Dion−Jacobson phase HLaNb$_2$O$_7$. *J. Mater. Chem.* **2012**, *22*, 11086−11092.

(27) Baerdemaeker, T. D.; Yilmaz, B.; Feyen, M.; Müller, U.; Vos, D. D. Interlayer expansion of RUB-36 with iron(III)chloride to obtain active alkylation catalysts. *Proceedings of the 17th International Zeolite Conference*; Moscow, Russia, July 7−12, 2013 ; International Zeolite Association, 2013; Vol. B, pp 37−38.

(28) Tsunoji, N.; Ikeda, T.; Ide, Y.; Sadakane, M.; Sano, T. Synthesis and characteristics of novel layered silicates HUS-2 and HUS-3 derived from a SiO$_2$−choline hydroxide−NaOH−H$_2$O system. *J. Mater. Chem.* **2012**, *22*, 13682−13690.

(29) Tada, H.; Jin, Q.; Nishijima, H.; Yamamoto, H.; Fujishima, M.; Okuoka, S.; Hattori, T.; Sumida, Y.; Kobayashi, H. Titanium(IV)

4620

dx.doi.org/10.1021/am500515p | *ACS Appl. Mater. Interfaces* 2014, 6, 4616−4621

Dioxide Surface-Modified with Iron Oxide as a Visible Light Photocatalyst. *Angew. Chem., Int. Ed.* **2011**, *50*, 3501−3505.

(30) Hattori, H.; Ide, Y.; Ogo, S.; Inumaru, K.; Sadakane, M.; Sano, T. Efficient and Selective Photocatalytic Cyclohexane Oxidation on a Layered Titanate Modified with Iron Oxide under Sunlight and CO_2 Atmosphere. *ACS Catal.* **2012**, *2*, 1910−1915.