An Inorganic–Organic Hybrid Possessing a Two-dimensional Ti–O Network and Surface Ethoxy Groups Prepared via a Reaction of Titanium Oxychloride with Lithium Ethoxide

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A new layered inorganic–organic hybrid possessing a Ti–O network has been prepared by a reaction between titanium oxychloride (TiOCl) and lithium ethoxide (LiOEt) at 120 °C for 7 days. The XRD analysis indicates that the interlayer distance of TiOCl increases from 0.80 to 1.19 nm, and the solid-state ^{13}C NMR spectroscopy and elemental analysis show partial substitution of ethoxy groups for chlorine atoms.

Inorganic–organic hybrids have been attracting increasing attention, and modification of inorganic compounds is a promising approach.[1] For inorganic layered compounds, besides intercalation reactions, interlayer surface modification via grafting reactions has been developed as an approach to preparing inorganic–organic hybrids.[1] Preparation of these graft-type hybrids requires reactive groups on the interlayer surface of inorganic layered compounds, and transition-metal oxyhalides possessing an FeOCl-type structure,[2] MOX (M = Fe, Ti, V, and Cr, X = Cl; M = In, X = Cl, Br, and I), are typical examples. Reactions of FeOCl with NH_3, CH_3NH_2,[3] methanol,[4] ethylene glycol,[5] sodium alkoxides,[6–8] potassium oxalate,[9] and potassium salt of 4-hydroxybenzoic acid[9] have been reported to date. As concerns TiOCl, a grafting reaction with ethylenediamine (en) was reported to yield a graft-type hybrid, $TiOCl_{0.5}(HNC_2H_4NH_2)_{0.5}$.[10] To the best of our knowledge, this is the only report on a grafting reaction involving TiOCl. Similar grafting reactions with NH_3[11] and en[10] were also reported for VOCl.

We report here on a grafting reaction of TiOCl using lithium ethoxide (LiOEt) to yield a layered inorganic–organic hybrid with a two-dimensional Ti–O network and surface ethoxy groups. Characterization by diffraction and spectroscopic techniques as well as by a morphology study is presented.

Manipulations for preparation of the product were performed under a protective nitrogen atmosphere using standard Schlenk techniques[12] or in a glove box filled with nitrogen. All the organic solvents used for reactions and washing procedures were distilled over appropriate drying reagents and then dried further using molecular sieve 3A.

TiOCl was prepared from a mixture of Ti_2O_3 (98%) and $TiCl_3$ (99.9%) (Ti_2O_3:$TiCl_3$ = 1:1.3 molar ratio) sealed in a quartz tube by heating at 650 °C for 7 days.[13] The crude product was washed with tetrahydrofuran under a nitrogen atmosphere. The XRD pattern (Rigaku RINT-2000 diffractometer with monochromated Cu Kα radiation) of the product (Figure 1a) revealed the formation of single-phase TiOCl with lattice parameters of $a = 0.3781(2)$, $b = 0.3360(1)$, and $c = 0.8041(3)$ nm, which showed good consistency with the reported values ($a = 0.379$, $b = 0.338$, and $c = 0.803$ nm).[13] The amount of titanium determined by inductively coupled plasma emission spectrometry (ICP; Varian Vista-MPX) after dissolution with hot aqua regia, 48.0%, and the amount of chlorine determined by means of ion chromatography (IC; Dionex, IC25) after treatment with 25 mass % NH_4OH, 34.8%, were consistent with the theoretical values of TiOCl (Ti, 48.2%; Cl, 35.7%).

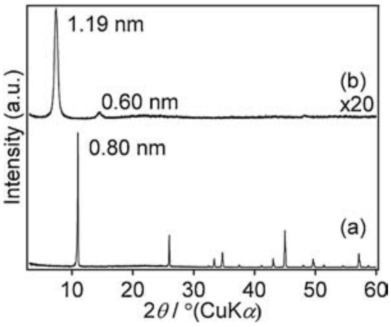

Figure 1. XRD patterns of (a) TiOCl and (b) the product of the reaction between TiOCl and LiOEt.

TiOCl, LiOEt [prepared from Li (99%) and distilled ethanol], and ethanol were sealed in an autoclave under a nitrogen atmosphere and allowed to react at 120 °C for 7 days (TiOCl: LiOEt = 1:1.3 molar ratio). The resulting product was washed with acetone and then dried further under reduced pressure.

When TiOCl was heated in ethanol at reflux, no reaction proceeded. Upon reaction with LiOEt, on the contrary, the color of TiOCl changed from lustrous brown to lustrous gray. In the XRD pattern of the product of the reaction between TiOCl and LiOEt (Figure 1b), the 001 reflection of TiOCl at $d = 0.80$ nm essentially disappears and a new reflection is present at $d = 1.19$ nm with a higher order ($d = 0.60$ nm). When EtOH was distilled from the washings, a solid residue was obtained, and this was identified as LiCl by XRD.

The morphology of the product was investigated by SEM (JEOL JSM-6390LV) as shown in Figure 2. TiOCl exhibits plate-like morphology, which is preserved upon the reaction of

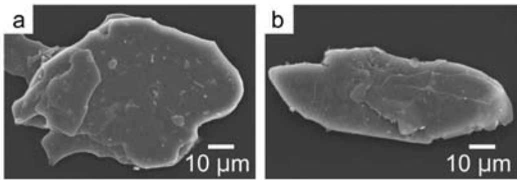

Figure 2. Scanning electron micrographs of (a) TiOCl and (b) the product of the reaction between TiOCl and LiOEt.

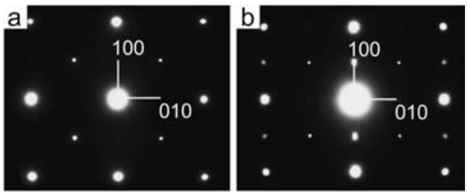

Figure 3. SAED patterns of (a) TiOCl and (b) the product of the reaction between TiOCl and LiOEt.

TiOCl with LiOEt. Thus, the shape of particles is unchanged during the reaction with LiOEt.

The structure of the product was further investigated by selective area electron diffraction (SAED, JEOL JEM-101, Figure 3). The SAED pattern of TiOCl along the [001] zone axis (the incident electron beam was perpendicular to the lateral plane of the plate-like particles) can be indexed based on an orthorhombic cell with a and b parameters similar to those determined by XRD ($a = 0.41$ nm, $b = 0.33$ nm). The absence of ($hk0$) spots with $h + k \neq 2n$, such as (100) and (010) spots, is well consistent with the extinction rule for the space group of TiOCl (*Pmmn*, No. 59).[13] In the SAED pattern of the product, which was also taken with the incident beam perpendicular to the lateral plane of the plate-like particle, all the spots observed in the SAED pattern of TiOCl are present in essentially the same positions, indicating the preservation of the layer structure. It is also clearly demonstrated that additional spots, which are forbidden for *Pmmn*, appear; the symmetry lowering also occurs simultaneously.

In the liquid-state ^{13}C NMR spectrum (JEOL JNM Lambda-500 at 125.40 MHz) of LiOEt (Figure 4a), two signals are present at 20.9 and 57.8 ppm. In the solid-state ^{13}C CP/MAS NMR spectrum (JEOL CMS-400 at 100.54 MHz) of the product (Figure 4b), the α carbon signal is present in a shifted position (71 ppm), while the position of the β carbon signal (19 ppm) is similar to that of LiOEt. It is worth noting that the chemical shifts of the product are closely similar to those reported for $Ti(OEt)_3$ possessing ethoxy groups bound to trivalent titanium (68.5, 66.7, and 21.4 ppm).[14] Thus, we conclude that the ethoxy groups are directly bound to Ti.

On the basis of these results, the reaction should be expressed as the following substitution reaction with respect to the Ti–Cl bond:

$$\mathrm{Ti{-}Cl + LiOEt \rightarrow Ti{-}OEt + LiCl} \qquad (1)$$

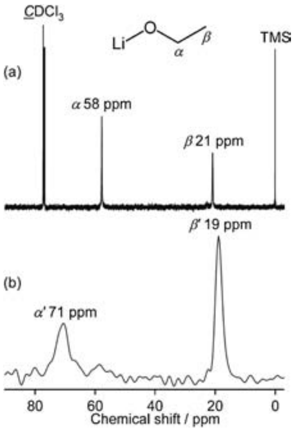

Figure 4. Carbon-13 NMR spectra: (a) liquid-state ^{13}C NMR spectrum of LiOEt and (b) solid-state ^{13}C CP/MAS NMR spectrum of the product of the reaction between TiOCl and LiOEt.

Since the broad weak ν(OH) band is present in the IR spectrum of the product at $\approx$3330 cm^{-1} (not shown), the hydroxy groups should also be present, probably owing to hydrolysis occurring during and/or after the aforementioned substitution reaction (TiOCl is not highly moisture-sensitive). On the basis of the ICP (Ti, 44.9 mass %), IC (Cl, 12.4 mass %), and elemental analyses (H, 2.9 mass %; C, 12.6 mass %) results, the composition of the product is estimated to be $TiOCl_{0.4}(OEt)_{0.5}(OH)_{0.1}$. The presence of three different groups or atoms (Cl, OEt, and OH) should result in the symmetry lowering, which is clearly demonstrated by the SAED pattern of the product (Figure 3). The increment along the stacking direction (0.39 nm) is very similar to that observed for the ethoxy derivative of FeOCl, $FeOCl_{0.40}(OEt)_{0.45}(OH)_{0.15}$ (0.40 nm),[8] indicating a bilayer arrangement of ethoxy groups in the present study.

In conclusion, we have demonstrated that TiOCl can undergo a grafting reaction with LiOEt via substitution of Cl with ethoxy groups. This approach could provide various inorganic–organic hybrids from TiOCl.

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