Synthesis of titanium tetraalkoxides from hydrous titanium dioxide and dialkyl carbonates

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The reaction of hydrous titanium dioxide ($TiO_2 \cdot nH_2O$, $n=0.15$–1.23) and dialkyl carbonates at 453–573 K offers a convenient synthetic method for titanium tetraalkoxides which are free from chlorine-containing impurities. Thus, hydrous titanium dioxide was almost completely converted into $Ti(OEt)_4$ by its reaction with diethyl carbonate at 493 K for 16 h. The reaction proceeded faster in the presence of a sodium hydroxide catalyst. From the hydrous titanium dioxide and dipropyl carbonate, $Ti(OPr^n)_4$ was obtained in a high yield.

Metal alkoxides are important chemicals as starting materials for preparing ceramics by the sol–gel method. One of the methods to prepare metal alkoxides is the reaction of metal chloride with an alcohol or with sodium alkoxide.[1]

Metal oxides could be starting materials for chlorine-free synthesis of metal alkoxides, if they were reactive enough towards appropriate organic compounds. The reactivity of a metal oxide, silicon dioxide, has been demonstrated. Rosenheim *et al.*[2] reported the transformation of silica into hexacoordinated dianion complexes using pyrocatechol as a complexing agent under basic conditions. Laine *et al.*[3,4] reported the formation of pentacoordinated silicates from silica, ethylene glycol and a base. Silicon alkoxides can be obtained by the reaction of silica with alcohols such as ethanol using potassium hydroxide as a catalyst under the conditions where water is continuously removed by azeotropic distillation.[5] Ono and coworkers[6–8] reported that silicon alkoxides can be easily synthesized by the reactions of silica gel with gaseous dialkyl carbonates in the presence of an alkali hydroxide [eqn. (1)].

$$SiO_2 + 2ROC(=O)OR \rightarrow Si(OR)_4 + 2CO_2 \ (R = Me, Et) \quad (1)$$

In this work, we report the synthesis of titanium tetraalkoxides by the reaction of hydrous titanium dioxide ($TiO_2 \cdot nH_2O$, $n=0.15$–1.23) with dialkyl carbonates. The reaction is given by eqn. (2).

$$TiO_2 \cdot nH_2O + (2+n)R'OC(=O)OR' \rightarrow Ti(OR')_4 + (2+n)CO_2 + 2nR'OH \ (R' = Et, Pr^n) \quad (2)$$

This reaction offers a simple method to synthesize chlorine-free titanium tetraalkoxides.

Experimental

Hydrous titanium dioxide was prepared as follows. To a 160 cm^3 portion of an aqueous solution of titanium(IV) sulfate, with stirring, was added dropwise aqueous ammonia until the pH reached 7.0. After the suspension of the precipitate was kept stirring overnight at a constant pH of 7.0, the precipitate was separated by filtration, washed with water four or five times, and then dried in an ambient atmosphere at 383 K for 1–18 h. The hydrous titanium dioxide ($TiO_2 \cdot nH_2O$) thus obtained had n in the range 0.15–1.23 depending on the drying time, as determined by thermal gravimetric analysis.

When a catalyst, for instance, sodium hydroxide, was used, a 5 mass% portion (based on TiO_2) of the catalyst was supported by an impregnation method: hydrous titanium dioxide was immersed for 1 h in an aqueous solution of the catalyst (as small an amount of water as possible), followed by heating under reduced pressure at 303 K to dryness and then at 353 K. The value of n did not change by this catalyst-loading procedure.

A 20 mmol portion of hydrous titanium dioxide (1.96 g for $n=1$) and diethyl carbonate (24.4 cm^3, 200 mmol) were introduced into a 120 cm^3 autoclave. After the atmosphere was replaced with nitrogen, the autoclave was heated to the desired temperature at a heating rate of 90 K h^{-1} and reactions were conducted under autogenous pressure with stirring. After cooling, the reaction mixture was transferred into a round-bottomed flask (capacity 50 cm^3) in a nitrogen atmosphere, and titanium tetraethoxide was separated by distillation under reduced pressure. The product thus isolated was weighed to determine its yield. The product, titanium tetraethoxide, was identified by ^{1}H NMR and IR absorption spectroscopy.†

For the reactions of hydrous titanium dioxide with dipropyl carbonate, the same reaction and analytical procedures as those with diethyl carbonate were adopted, except that the amounts of hydrous titanium dioxide and dipropyl carbonate charged into the autoclave were 15 mmol (1.47 g for $n=1.0$) and 23.2 cm^3 (150 mmol), respectively.

Results and Discussion

Reaction of hydrous titanium oxide with diethyl carbonate

(*a*) Effect of reaction temperature. The reaction of hydrous titanium dioxide ($TiO_2 \cdot H_2O$) with diethyl carbonate was carried out at various temperatures for 16 h. Fig. 1 shows the yield of titanium tetraethoxide, $Ti(OEt)_4$, as a function of reaction temperature. At 433 K, $Ti(OEt)_4$ was not obtained. At 453 K, the yield was 77% and reached *ca.* 95% at 493 and 533 K. The yield slightly decreased at 573 K. Thus, in the temperature range 493–533 K, practically complete conversion of hydrous titanium dioxide to $Ti(OEt)_4$ can be attained.

Fig. 2 shows the change in the yield of $Ti(OEt)_4$ with reaction time at 453 and 493 K. At 453 K, the presence of the induction time was clear. The yield was almost negligible over the first 4 h, and then sharply increased with reaction time to reach *ca.* 60% at 10 h. The yield only slightly increased to 65% by

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† The IR spectrum for the product obtained in this work is in agreement with that of the published data (*The Aldrich Library of FT-IR Spectra Edition 1*, vol. 1, ed. C. J. Pouchert, 1985), except that several minor bands in the published spectrum are missing. Titanium tetraethoxide containing chlorine-containing impurities from a commercial source, which had been produced from titanium tetrachloride, showed these minor bands together with the bands observed for the product obtained in this work. This indicates that the bands which are missing for the sample prepared in this work are probably attributed to chlorine-containing titanium species.

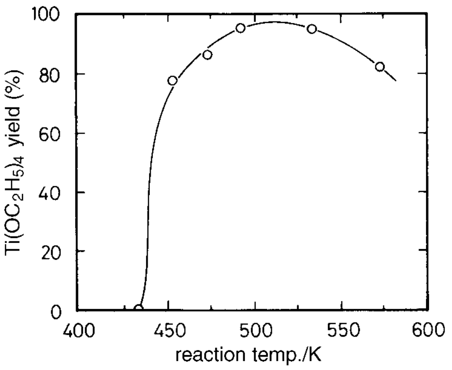

Fig. 1 Reaction-temperature dependence of the titanium tetraethoxide yield. Reaction conditions: $TiO_2{\cdot}nH_2O$ ($n=1.0$) 1.96 g (20 mmol based on TiO_2), diethyl carbonate 24.4 cm^3 (200 mmol), and reaction time 16 h.

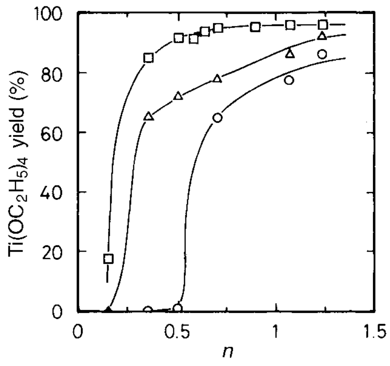

Fig. 3 Effect of n-value in $TiO_2{\cdot}nH_2O$ on the titanium tetraethoxide yield. Reaction conditions: $TiO_2{\cdot}nH_2O$ 1.65–2.04 g (20 mmol based on TiO_2), diethyl carbonate 24.4 cm^3 (200 mmol), reaction time 16 h, and reaction temperature 453 K (○), 473 K (△) and 493 K (□).

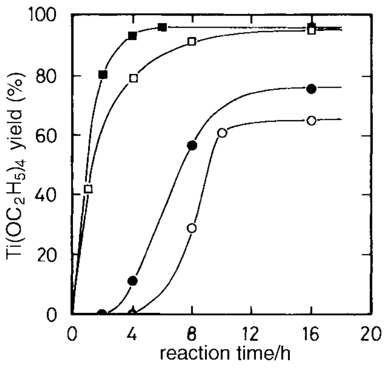

Fig. 2 Time course of the titanium tetraethoxide yield in the presence and absence of sodium hydroxide catalyst. Reaction conditions: $TiO_2{\cdot}nH_2O$ ($n=0.70$) 1.85 g (20 mmol based on TiO_2), diethyl carbonate 24.4 cm^3 (200 mmol), and reaction temperature 453 K (○, ●) and 493 K (□, ■). Open and closed symbols represent the yield obtained for the reactions in the absence and presence of 5 mass% of a sodium hydroxide catalyst, respectively.

further increasing the reaction time to 16 h. The presence of an induction time indicates that the reaction proceeds through an intermediate rate (or species) before the monomeric $Ti(OEt)_4$ is finally formed. At 493 K, no induction period was observed. The yield monotonously increased with reaction time, and reached 95% at 16 h.

(*b*) Effect of dehydration of hydrous titanium dioxide. The effect of the extent of dehydration of hydrous titanium dioxide ($TiO_2{\cdot}nH_2O$) on the yield of $Ti(OEt)_4$ was examined. The extent of dehydration was varied by changing the time of drying the samples at 383 K, with n varying from 0.15 to 1.23. The reactions were carried out at 453, 473 and 493 K for 16 h. As shown in Fig. 3, at each reaction temperature, higher yields of $Ti(OEt)_4$ were obtained with samples with higher n, *i.e.* with lower degree of dehydration.

(*c*) Effect of the catalysts. In the reaction of silica gel with dialkyl carbonates, alkali-metal hydroxides and halides are effective catalysts.[6,7] Therefore, these compounds were tested as catalysts for the reaction of hydrous titanium dioxide with diethyl carbonate. After the catalysts were supported by 5 mass%, the reactions were carried out at 493 K for 4 h. When the catalyst was LiOH, NaOH, KOH and CsOH, the yield of $Ti(OEt)_4$ was 91, 93, 90 and 82%, respectively, while the reaction using no catalyst gave a 79% yield. All the alkali-metal hydroxides examined showed a promoting effect. Alkali-metal chlorides, NaCl and KCl, exhibited a retarding effect, the yield being 72 and 71%, respectively. Sodium hydroxide is the most effective catalyst.

Fig. 2 also shows the time courses of the $Ti(OEt)_4$ yield obtained for the reactions using the NaOH catalyst. Here the promoting effect of NaOH is clearly seen; at 453 K, the induction time was shortened, and higher yields of $Ti(OEt)_4$ were obtained. At 493 K, a very high yield of 96% was attained after only 6 h.

(*d*) Effect of diethyl carbonate/hydrous titanium dioxide ratio. The effect of the molar ratio of diethyl carbonate to hydrous titanium dioxide ($TiO_2{\cdot}nH_2O$, $n=0.94$) on the $Ti(OEt)_4$ yield was examined. The reactions were carried out at 503 K for 4 h and the results are shown in Fig. 4. Without a catalyst, a high molar ratio of 10 was required to obtain a high yield of $Ti(OEt)_4$. Upon loading NaOH as a catalyst on hydrous titanium dioxide, a molar ratio of 6 was sufficient to obtain a high yield.

Hydrous titanium dioxide is considered to consist of flocculates of small anatase crystals[9] and the structure of hydrous titanium dioxide is schematically shown in Fig. 5.[10] It contains a number of hydroxy groups as well as water molecules coordinated to titanium ions.

Under the reaction conditions, the hydroxy groups on the surface may react with diethyl carbonate to form ethoxy

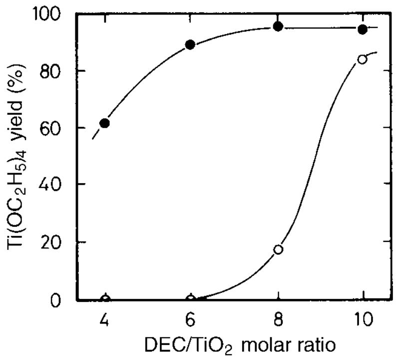

Fig. 4 Effect of molar ratio of diethyl carbonate (DEC) to hydrous titanium dioxide on the titanium tetraethoxide yield. Reaction conditions: $TiO_2{\cdot}nH_2O$ ($n=0.94$) 0.484 g (5 mmol based on TiO_2), diethyl carbonate 2.4–6.1 cm^3 (20–50 mmol), reaction time 4 h, and reaction temperature 503 K. Open and closed symbols represent the yield obtained for the reactions in the absence and presence of 5 mass% of a sodium hydroxide catalyst, respectively.

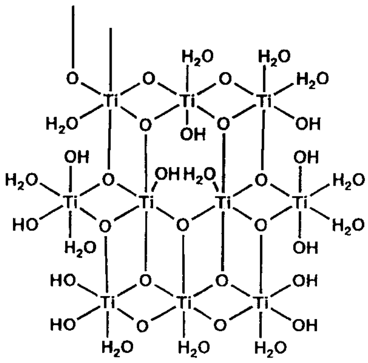

Fig. 5 Structure of hydrous titanium dioxide[10]

groups, ethanol and carbon dioxide [eqn. (3)].

$$\text{Ti}{-}\text{OH}+\text{EtOC}(=\text{O})\text{OEt}\rightarrow\text{Ti}{-}\text{OEt}+\text{EtOH}+\text{CO}_2 \quad (3)$$

The water molecules coordinated to titanium ions readily react with diethyl carbonate to give ethanol and carbon dioxide.

$$\text{H}_2\text{O}+\text{EtOC}(=\text{O})\text{OEt}\rightarrow 2\text{EtOH}+\text{CO}_2 \quad (4)$$

By these reactions, the hydroxy groups and the water molecules in hydrous titanium dioxide are scavenged as ethanol, and the reaction system is always kept free from water, which may promote the recondensation of the alkoxide product, $Ti(OEt)_4$.

Synthesis of titanium tetrapropoxide

Hydrous titanium dioxide ($TiO_2 \cdot nH_2O$, $n = 0.70$) reacted with dipropyl carbonate to afford titanium tetrapropoxide, $Ti(OPr^n)_4$. The reaction at 493 K for 16 h without catalyst gave an 84% yield of $Ti(OPr^n)_4$. When sodium hydroxide was used as a catalyst (5 mass%), reaction at 493 K for 6 h gave a yield of 92%. The product was identified by IR and ^1H NMR spectra.

Conclusion

Titanium tetraethoxide (or tetrapropoxide) is prepared by the reaction of hydrous titanium dioxide and diethyl (or dipropyl) carbonate. The reaction proceeds almost to completion at 493–533 K after 16 h. Titanium tetraalkoxide is formed by the successive cleavage of Ti—O—Ti bonds in hydrous titanium dioxide by reaction with dialkyl carbonate molecules with formation of Ti—OEt bonds and release of carbon dioxide. Use of a catalyst such as sodium hydroxide remarkably reduces the time required to accomplish the reaction. Reaction of the catalyst with hydrous titanium dioxide presumably occurs, giving rise to the cleavage of the Ti—O—Ti bond and simultaneously, the formation of a Ti—OEt bond. The catalyst may facilitate the formation of an EtO group from a diethyl carbonate molecule, which attacks the Ti—O—Ti bond to form the Ti—OEt bond.

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