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Low Temperature Synthesis of TiO_2 by Vapor-Phase Hydrolysis of Titanium Isopropoxide

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At sufficiently high H_2O concentration, titanium isopropoxide vapor could almost completely be hydrolyzed to form submicron-size TiO_2 powder at a reaction temperature as low as 380 K with little deposition inside a tubular-flow reactor, indicating a highly efficient method for preparation of powders.

It has been reported that pyrolysis or hydrolysis of vapors of titanium alkoxides can yield fine TiO_2 powders at 850 - 1300 K.[1-2] The efficiency of powder preparation processes depends significantly on the reaction temperature and the yield of powder to the reactant supplied. Although the use of $Ti(iso\text{-}OC_3H_7)_4$ remarkably decreased the pyrolysis temperature to 523 K,[3-4] production of the particles by this process was inefficient due to heterogeneous decomposition of the alkoxide on the reactor wall.[5] This letter describes a vapor-phase hydrolysis reaction of $Ti(iso\text{-}OC_3H_7)_4$ that successfully produces uniform, submicron-size particles of TiO_2 at low temperatures with high yield.

Titanium isopropoxide was hydrolyzed in a tubular reactor (ID= 1.26 cm, L= 51 cm) at atmospheric pressure. Two He streams separately carried the vapors of H_2O and $Ti(iso\text{-}OC_3H_7)_4$ from temperature-controlled evaporators. The $Ti(iso\text{-}OC_3H_7)_4$ stream was fed to the main reactor from the inner pipe (ID= 0.2 cm) of a nozzle system consisting of two concentric pipes. Pure He stream was supplied from the outer pipe (ID= 0.55 cm) to keep the nozzle tip from plugging due to deposition of TiO_2. The volumetric flow rate ratio of the H_2O, pure He and $Ti(iso\text{-}OC_3H_7)_4$ streams was 1.0/1.02/1.87. Inlet $Ti(iso\text{-}OC_3H_7)_4$ concentration was 0.64% and inlet H_2O concentration was 4.54% or 44.6% at the nozzle tip, located 6 cm inside the inlet of the reactor. The gas residence time in the reactor was 2.3 s. The particles were

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collected by a membrane filter heated to 423 K. The amount and morphology of the TiO_2 deposits were determined by inserting glass rings (OD= 1.2 cm, ID= 1 cm, L= 2 cm) inside the reactor between the inlet and the filter.

The stoichiometry of the pyrolysis reaction is[3-4]:

$$Ti(iso\text{-}OC_3H_7)_4 \longrightarrow TiO_2.nH_2O + 4C_3H_6 + (2-n)H_2O \qquad (1)$$

The following stoichiometric relation is expected for the hydrolysis reaction:

$$Ti(iso\text{-}OC_3H_7)_4 + (2+n)H_2O \longrightarrow TiO_2.nH_2O + 4iso\text{-}C_3H_7OH \qquad (2)$$

TiO_2 itself is a well-known catalyst for dehydration of alcohols.[6] Therefore:

$$iso\text{-}C_3H_7OH \xrightarrow{TiO_2} C_3H_6 + H_2O \qquad (3)$$

Concentrations of H_2O, C_3H_6 and iso-C_3H_7OH in the exit stream for 4.54% H_2O concentration experiments were determined by gas chromatograph after filtration and separation of condensable species. The molar ratios of C_3H_6 to iso-C_3H_7OH were 1%, 9%, and 100% at reaction temperatures of 380 K, 477 K, and 688 K respectively at the end of 60 min. These results indicated that pyrolysis was insignificant at temperatures lower than 477 K. This conclusion was further confirmed by an experiment in which the conversion of $Ti(iso\text{-}OC_3H_7)_4$ was less than 5% at 0% H_2O concentration and 477 K. Figure 1 shows the result of gas analysis with time. Decrease in iso-C_3H_7OH concentration with time was presumably due to the TiO_2 accumulation in the reactor which converts the alcohol to propylene by Eq. 3. The conversions of $Ti(iso\text{-}OC_3H_7)_4$ were 89% (380 K), 95% (477 K), and 100% (688 K). Thermal desorption analysis and TGA (up to 973 K) of the collected particles indicated C_3H_6 and H_2O as volatile species (Table 1). Amount of C_3H_6 corresponded to 3.6% (380 K), 3.1% (477 K), and 0.14% (688 K) of the inlet $Ti(iso\text{-}OC_3H_7)_4$ concentration. (A possible source of C_3H_6 was adsorbed iso-C_3H_7OH, which can catalytically dehydrate on the surface of TiO_2 by heating). Consequently, the hydrolysis reaction almost reached completion under all the conditions studied here.

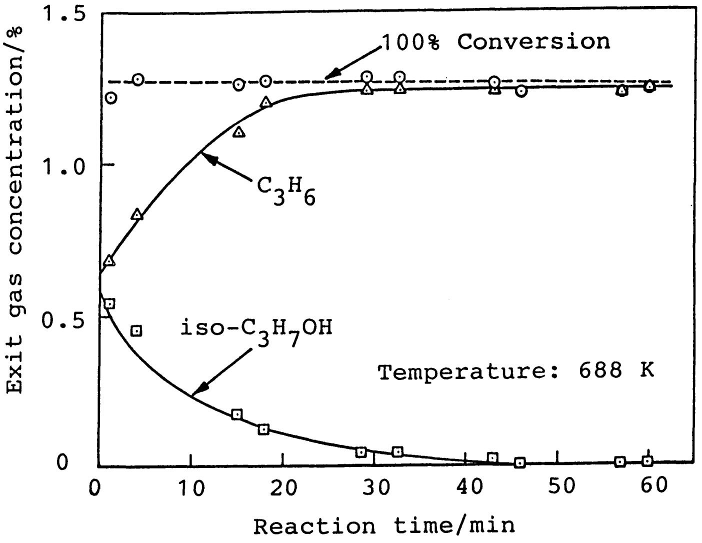

Fig. 1. Analysis of the exit gas. Inlet H_2O concentration was 4.54%.

The particles were amorphous,

porous (BET surface area: 55-228 m^2/g), spherical and highly pure (carbon content< 1 wt%). Detection of the H_2O desorption from the particles up to 626 K suggested that they were hydrous. The value of n, in $TiO_2.nH_2O$, was suggested as between 0.5 and 1.0 for the TiO_2 powders prepared by the hydrolysis of the titanium alkoxide solutions[7] which corresponds the H_2O content of the present particles synthesized at 380 and 477 K (Table 1). Particle size decreased with increasing temperature and H_2O concentration (Table 1). Particle size distributions were narrow, showing a small geometric standard deviation ranging between 1.15 - 1.27. Details of the particle properties will be presented elsewhere.[8]

The reactor can be divided into three imaginary zones with respect to amount and morphology of the deposits on the reactor wall (Table 1). The SEM micrographs of the deposits (Fig. 2) suggested that the deposition in zone 1 was fused particles possibly deposited by diffusion and subsequently enlarged by chemical or physical vapor deposition. The amount of deposition in zone 2 was negligible. The radial temperature gradient at the exit of the reactor caused thermophoretic deposition of particles in zone 3 as was previously observed in pyrolysis of Ti(iso-$OC_3H_7)_4$.[5] The increase of both reaction temperature and H_2O concentration significantly decreased the reactor wall deposition in zone 1. While the mechanism is not fully understood, it is presumed that the reaction rates, increased by these fac-

Table 1. Variation of deposition with inlet H_2O concentration and temperature.

Inlet H_2O concn. (%)	T / K	Zone 1[a] (%)	Zone 2[a] (%)	Zone 3[a] (%)	Particles on filter[a] (%)	Mass balance of TiO_2[b] (%)	Particle size / nm	Volatile species H_2O (wt%)	Volatile species C_3H_6 (wt%)
4.54	380	45	1	0	54	94	92	10.7	7.4
4.54	477	30	3	4	63	98	71	12.1	6.2
4.54	688	2	5	9	84	90	33	3.7	0.3
44.60	380	2	2	0	96	95	61	14.0	2.3
44.60	477	2	2	4	92	94	41	17.8	<0.1
44.60	688	1	1	9	89	85	16	5.6	<0.1

a) Results are on dry TiO_2 basis. Zone 1 is the first 16 cm of the reactor beyond the nozzle tip (there was negligible deposition before the tip). Zone 2 is between 16 - 39 cm. Zone 3 is between 39 - 45 cm, before the filter.

b) The fraction of TiO_2 collected to that fed to the reactor.

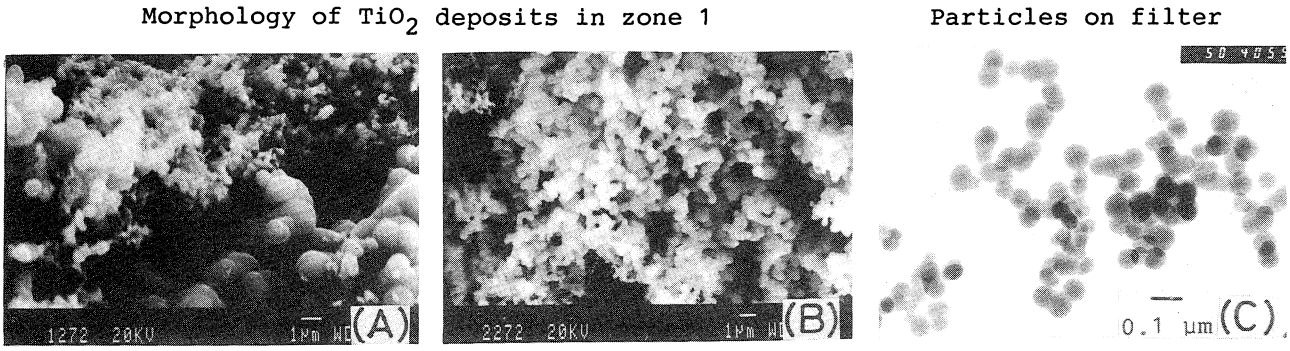

Fig. 2. SEM micrographs of the TiO_2 deposits on the reactor wall in zone 1. Samples were taken between (A) 0 - 2 cm, (B) 4 - 6 cm beyond the nozzle tip (size of the spheroidal units is around 65 nm). (C) TEM micrograph of the particles (particle size is 71 nm). Temperature was 477 K. Concentration of H_2O was 4.54%.

tors, confined the reaction zone to the vicinity of the nozzle tip and subsequently reduced the diffusive flux of the particles as well as the reactant vapor toward the wall.

An important result of this investigation is given in Table 1. Mass balance determined that, at high H_2O concentration, almost all the $Ti(iso\text{-}OC_3H_7)_4$ supplied to the reactor was converted to TiO_2 powder with little deposition inside the reactor at a reaction temperature as low as 380 K. By contrast, in pyrolysis of $Ti(iso\text{-}OC_3H_7)_4$ at 573 K, 30 - 50% of TiO_2 deposited on the reactor wall in zone 1 as a film due to heterogeneous initiation of the reaction. Homogeneous initiation of the reaction in the case of hydrolysis is responsible for the present successful results. It was therefore concluded that the hydrolysis of $Ti(iso\text{-}OC_3H_7)_4$ is a very promising process for low-temperature production of fine TiO_2 particles in the gas phase.

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