CHEMISTRY LETTERS, pp. 1283 - 1286, 1984.

PREPARATION OF POROUS, AMORPHOUS, AND ULTRAFINE TiO_2 PARTICLES BY CHEMICAL VAPOR DEPOSITION

Hiroshi KOMIYAMA,* Takashi KANAI, and Hakuai INOUE
Department of Chemical Engineering, Faculty of Engineering,
The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113

Ultrafine TiO_2 particles were prepared by chemical vapor deposition of titanium tetraisopropoxide. The particle formation reaction, being catalyzed by the TiO_2 deposit on the reactor wall, took place even at as low a temperature as 250°C, according to the stoichiometric relation of $Ti(C_3H_7O)_4 \longrightarrow TiO_2 + 4C_3H_6 + 2H_2O$. The TiO_2 particles were amorphous and porous, the specific surface area of which reached 300 m^2/g.

Chemical vapor deposition (CVD) is a process to deposit solids, in the form of a film or particles, using gaseous components. Extensive effort has been devoted to preparing ultrafine particles of metals, metal oxides and other inorganic compounds.[1] It is usual for the synthesis of particles by CVD method, to carry out the reaction at high temperatures in order to avoid incomplete reaction. Attempts were made to use metal organic compounds as the starting material in CVD, which may lower the reaction temperature.[2,3] One of the attractive features of the low temperature CVD is the possibility of producing a material possessing a structure which is unstable at high temperatures. This paper is concerned with the low temperature synthesis of TiO_2 particles from titanium tetraisopropoxide (TTIP). Emphasis is placed upon the catalytic effect of the reactor wall in the CVD process and the porous and amrophous structure of the prepared particles.

The reactor was a 3 cm glass tubing, equipped with a nozzle at the centerline. A helium stream flowed through a TTIP vaporizer, to which liquid TTIP was

supplied by a metering pump, and was introduced into the reactor from the nozzle. An electric heating system was used to keep the temperature of the reactor constant to within 10 °C within a zone extending 20 cm downstream of the nozzle. The effluent stream was sampled for analysis by gaschromatography, after flowing through a membrane filter followed by a fiber layer filter for collecting the particles. The major products in the gas phase were C_3H_6 and H_2O. Hence, the reaction rate was readily determined by the concentration of C_3H_6.

Figure 1 shows the fractional conversion of the supplied TTIP for an initial TTIP concentration of 0.6% and a total flow rate of 36.7 cm^3(STP)/s, as a function of temperature. When a reactor of clean wall was used, the reaction became detectable at around 370 °C. With increasing temperature, the reaction rate increased (line 2 in Fig. 1), until the conversion of TTIP abruptly increased up to 100% at a certain temperature. This abrupt increase of the TTIP conversion took place simultaneously with the depositon of TiO_2 on the reactor wall. Once the deposition of TiO_2 on the reactor wall occurred, the reaction took place much more rapidly even at lower temperatures, as shown in Fig. 1 (line 1). On the other hand, if the TiO_2 deposit was taken off, the reaction rate decreased down to line 2 in Fig. 1. Hence, it was concluded that the TiO_2 deposit on the reactor wall was responsible for the acceleration of the reaction.

The prepared particles were spherical as shown by the electron microscopic photographs. The average diameter of the particles depended slightly on the reaction temperature in the range of 0.2 to 0.4 μm. The specific surface area, as measured by the BET method at the boiling temperature of nitrogen, however, was much more strongly dependent on the reaction temperature as shown in Fig. 2. The particles prepared at

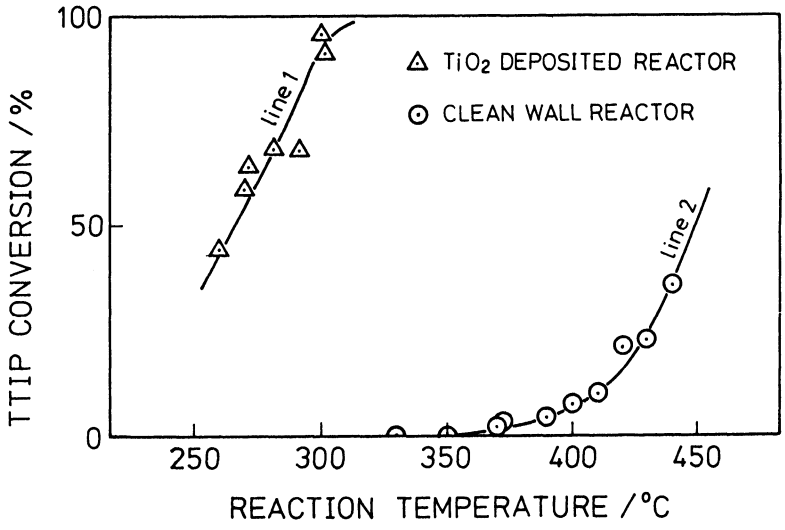

Fig. 1. Reaction rate dependence on temperature for TiO_2 deposited and undeposited reactors.

temperatures higher than 400 °C had a surface area of 20 to 30 m^2/g, which was 2 to 3 times larger than the outer surface area of the particle, based on their average diameter as determined by electron microscopy. The larger surface area of the particles prepared at lower temperatures is considered to be due to their highly porous structure. X-Ray diffraction analysis showed that the particles prepared above 400 °C are anatase but that the particles prepared below 320 °C are amorphous.

The properties of the amorphous and highly porous particles, prepared at 290 °C, were further examined. IR absorption spectrum showed no evidence of impurities, except the absorption due to adsorbed water. Differential thermal analysis showed two exothermic peaks, a broad and small peak at around 250 °C and a sharp and large peak at 390 °C. X-Ray diffraction patterns of the particles, treated at 110, 260, and 450 °C, showed a halo, no peaks and the peaks corresponding to anatase, respectively. The BET surface area of these particles are 300, 250, and 11 m^2/g, respectively. These analytical results indicate the possibility that the

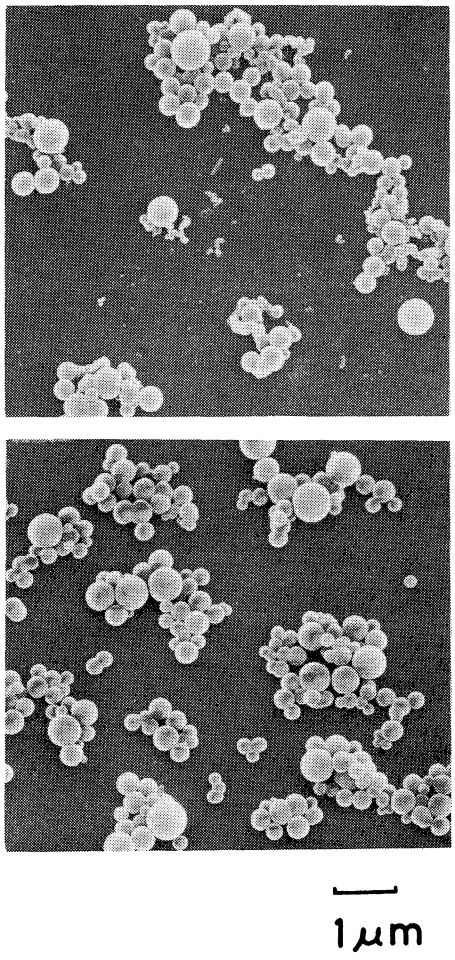

Fig. 3. Scanning electron micrographs.
a) Particles prepared at 500 °C: the average diameter is 0.26 μm.
b) Particles prepared at 320 °C: the average diameter is 0.29 μm.

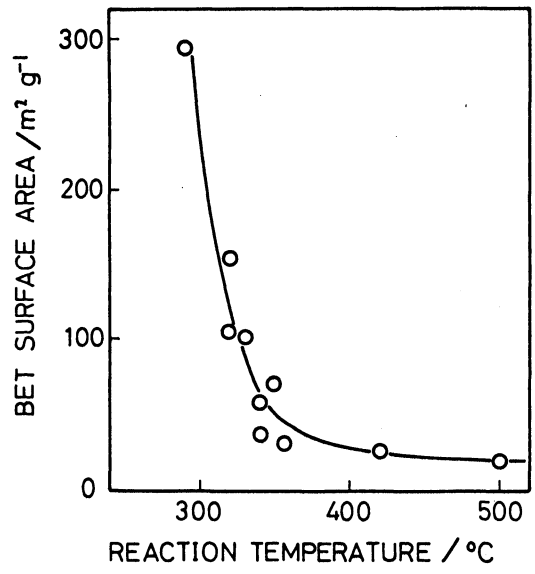

Fig. 2. Dependence of specific surface area on reaction temperature.

amorphous and porous structure of the particles are stable below 250 °C, that at around 250 °C crystallization occurs to yield crystalline structure, maintaining the porous structure and that at 390 °C the particles are sintered to become nonporous.

The synthesis of TiO_2 particles by means of the vapor phase reaction of $TiCl_4$ has been extensively studied.[4] Depending on the reacting conditions such as the reactant species, the temperature, the concentrations, and the residence time of the reactant species in the reactor, crystalline particles of anatase, rutile, or the mixture of anatase and rutile were produced. Formation of the amorphous phase by CVD method, however, has not been reported. The aqueous phase precipitation of amorphous and porous TiO_2 has been reported,[5] but the surface area could only be maintained by the addition of considerable amounts of sulfuric ions.[6] Further investigation into the physical and chemical properties of the TiO_2 particles prepared in this work and their formation mechanism is now under way. At the present stage of the investigation, it is concluded that the low temperature synthesis of oxide particles using alcoxides as starting materials will provide a new means for the preparation of amorphous and porous particles.

References

1) A. Kato, J. Soc. Powd. Tech. Jpn., 18, 36 (1981).

2) A. Kamata, S. Matsumoto, and N. Otsuka, Nippon Kagaku Kaishi, 1983, 1715.

3) K.S. Mazdiyasni, C.T. Lynch, and J.S. Smith, J. Am. Ceram. Soc., 48, 372 (1965).

4) Y. Suyama, K. Ohmura, and A. Kato, Nippon Kagaku Kaishi, 1976, 584.

5) K. Funaki and Y. Saeki, Kogyo Kagaku Zasshi, 59, 1291 (1956)

6) A. Kurosaki and S. Okazaki, Nippon Kagaku Kaishi, 1976, 1816.

(Received April 14, 1984)