Study of the Nature of Water in Rutile by Slow-Neutron Inelastic Scattering

Studies on the nature of bound as well as adsorbed water present in the bulk and at the surface of many hydrates and precipitated oxides are of primary importance in understanding the behavior and surface chemistry of numerous colloidal systems. The degree of hydration and the extent to which functional groups such as OH cover the surface and the ease with which these adsorbed molecules and functional groups can be removed is also important in determining the catalytic properties of the surface.

The nature of water adsorbed on rutile TiO_2 has been the subject of several investigations. For example, the effect of traces of adsorbed water on dispersibility and stability of dispersions is well known (*1*, *2*). It has been pointed out that a small part of water present in rutile is irreversibly adsorbed (*3*), and that surface water rather than "osmotically" bound water is evolved on ignition (*4*, *5*). Infrared, thermogravimetric, and heats of immersion studies have also been performed (*6*, *7*, *11*, *12*).

In the present work an attempt is made to elucidate the nature and type of water present in rutile by means of thermal-neutron scattering. Because the scattering of thermal neutrons reflects the dynamic as well as the structural nature of materials, specific information not obtainable by other techniques can be deduced from the momentum and energy transfer that the neutron undergoes in elastic or inelastic scattering processes. The neutron scattering cross section for hydrogen is very large (~80 barns) compared to that of other atoms and almost entirely incoherent, so that studies of diffusive and vibrational motions and identification and characterization of hydrogenous groups in the bulk and at the surface of polycrystalline samples is possible.

A review of the application of thermal-neutron scattering to studies of colloidal systems and surfaces has been presented in ref. (*8*).

EXPERIMENTAL

The present experiments utilized the "cold"-neutron time-of-flight spectrometer at the Army Materials and Mechanics Research Center Research Reactor. This type of spectrometer has been described in detail elsewhere (*9*). In this apparatus the neutron spectrum from the reactor is filtered through 16 inches of refrigerated beryllium so that a quasimonochromatic beam of neutrons of energy less than 42 cm^{-1} and width at half-maximum of ~15 cm^{-1} is incident on the scatterer. The filtered neutrons impinge upon the sample and are scattered either elastically (no change in energy) or inelastically (gain energy from thermally populated energy states in the sample). The energy spectrum of the scattered neutrons is determined by chopping the scattered beam and measuring the time-of-flight at a scattering angle of 90°. The observed spectrum is then corrected for background, chopper transmission, counter efficiency, and window scattering to obtain the true energy distribution.

The sample was contained in an aluminum cell shielded with cadmium to minimize background scattering. The cell could be connected through a metal–Pyrex joint and a stopcock to a vacuum line and the sample outgassed. A vacuum of 10^{-6} torr was possible in the system.

The rutile samples used in the investigation were obtained from National Lead Company Titanium Division, South Amboy, N. J. The high-area sample was prepared by addition of $TiCl_4$ to aqueous ammonia. After heating the mixture for 30 min to 85° and cooling to 25°, the pH was adjusted to 6.5 and the mixture was filtered. The precipitate was then washed with distilled water until free of Cl$^-$ and the residue was dried in air at 120° for 2 hr. The surface area as determined by the BET method was 160 m^2/g. A second sample of rutile prepared by a similar method but dried at 1200°C for 2 hr had a surface area of 0.5 m^2/g and an impurity content of 5 ppm. X-Ray diffraction studies showed only the presence of crystalline rutile.

Results and Discussion

The neutron time-of-flight spectrum for the high-area rutile sample (160 m^2/g) exposed to air for several days is shown in Fig. 1 (a). Removal of water from the sample by outgassing at 200°C for 24 hr results in the spectrum shown in Fig. 1 (b). High-temperature ignition of these samples gave 92.2 and 98.5 wt% rutile on ignition, respectively. The surface area of the sample following outgassing at 200°C as obtained by the BET method in a similar but separate experiment was 100 m^2/g.

In the neutron spectrum it is necessary to distinguish between the scattering from the bulk or substrate material and that from the adsorbate. Although the scattering cross sections of Ti and O are much smaller than that of hydrogen, their contribution is important since their number is much greater than the number of "sorbed" hydrogens. However, assuming a monolayer of adsorbed water, the ratio of the contribution to the observed spectrum from the bulk material (neglecting possible absorbed water) to that from surface water is calculated to be 0.45. The major contribution to the spectrum in the case of the high-area sample is therefore expected to come from surface water.

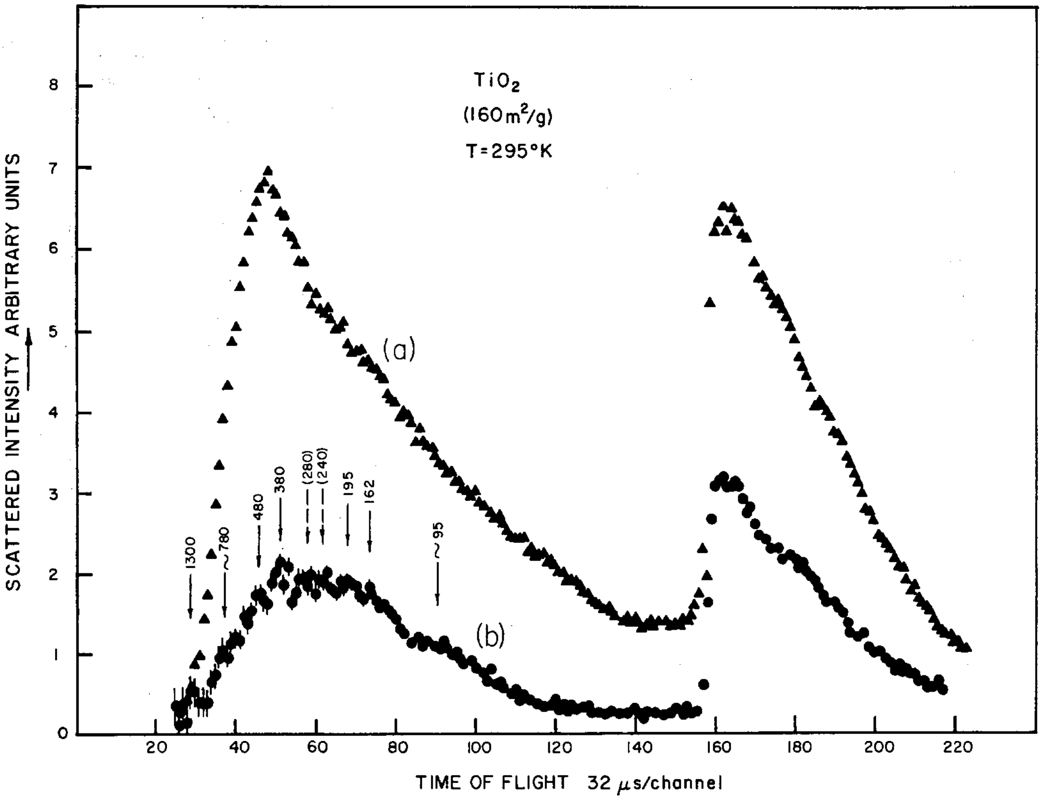


FIG. 1. Neutron time-of-flight spectra of high-area rutile (160 m^2/g) after exposure to air for several days (a), and after outgassing the same sample for 12 hr at 200°C (b). Indicated vibrational frequencies are in cm^{-1}.

The neutron spectrum of the unactivated high-area sample of rutile is very similar to spectra obtained for alumina and silica exposed to air for several days (*10*). The presence of an intense peak centered at ~450 cm^{-1} and the overall similarity to the spectrum of liquid water indicates that considerable molecular water is present. The sharpness of the quasielastic peak compared to that of liquid water suggests, moreover, that this water has a lower mobility than molecules in liquid water.

Infrared measurements as a function of vacuum treatment at different temperatures by Lewis and Parfitt (*11*) and by Yates (*12*) have shown that the band at 1600 cm^{-1} assigned to the fundamental frequency ν_2 of water disappears on outgassing at 200°, indicating more or less a complete removal of strongly physisorbed water molecules. Thermogravimetric studies (*11*, *13*) on rutile also indicate a loss between 100° and 400°C of strongly held water and OH group condensation. On the other hand, the neutron spectrum of rutile, vacuum-treated at 200°C [Fig. 1(b)], indicates a possibly incomplete removal of molecular water as evidenced by the peak at 480 cm^{-1}.

The neutron spectrum of a rutile sample (sintered in air at 1200°) with a low surface area (~0.5 m^2/g) is shown in Fig. 2 (a). Reduction of this sample at 500°C for 2 hr in dry hydrogen yields a sample whose spectrum is shown in Fig. 2(b). The absence of a peak at 450–480 cm^{-1} in Fig. 2(a) indicates no molecular water either in the bulk or at the surface and is in accordance with the conclusions of Czanderna and Honig (*14*) that the entrapped water vapor is eliminated completely from TiO_2 at 800°C.

For the low-area samples the expected scattering from the bulk materials is more than two orders of magnitude greater than that from a monolayer of adsorbed water. These spectra therefore correspond to lattice modes of TiO_2 (rutile) and are in excellent agreement with the infrared results of Liebisch and Rubens (*15*) and of Waldron [as reported by von Hippel *et al.* (*16*)] and the Raman measurements of Narayanan (*17*). Waldron's infrared results show broad maxima at 600 and 260 cm^{-1} and a sharp peak at 410 cm^{-1}, whereas the neutron spectra show peaks at 790, 570, 405, 290, 195, and 90 cm^{-1}.

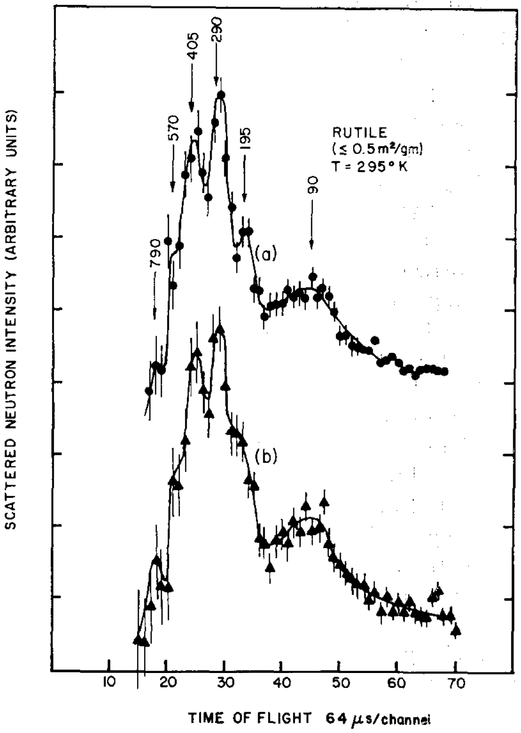
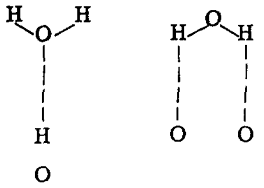


FIG. 2. Neutron time-of-flight spectra of low-area rutile (≃0.5 m^2/g) after sintering at 1200°C (a), and after reduction in hydrogen at 500°C for 2 hr of the sintered sample (b). Indicated vibrational frequencies are in cm^{-1}.

The differences in neutron spectra observed after reduction could arise from a chemically induced change in crystallographic structure. Ehrlich (*18*) and Assayug *et al.* (*19*) have found that the rutile structure of TiO_2 is maintained to stoichiometry of $TiO_{1.90}$. In the present experiment the stoichiometry of the reduced sample was approximately $TiO_{1.99}$ so that no change in structure occurs. Furthermore, the removal of oxygen would not be expected, by itself, to induce the observed spectral changes. The differences observed in the neutron spectrum of the reduced sample are attributed to vibrations involving hydrogen already present in the bulk enhanced by additional adsorbed hydrogen. Von Hippel (*16*) has concluded from his infrared studies of the OD and OH stretching region that hydrogen was present in the bulk of rutile. Two bands were observed for both ν_S(OD) and ν_S(OH) attributed to deutrons and protons trapped by O^{2-} and forming hydrogen bonds at two differing sites. Upon hydrogen reduction the transitions at 790 and 195 cm^{-1} observed in the neutron spectrum approximately double in intensity, suggesting added hydrogen, with the latter becoming very broad. These transitions are assigned as corresponding, respectively, to Ti–OH bending, in analogy with silica, (*10*) and OH- - -O stretching vibrations.

Further, the absence of peaks at 405 and 290 cm^{-1} in the activated high-area TiO_2 spectrum [Fig. 1(b)] confirms that the spectrum is due primarily to surface H_2O, rather than lattice modes. The shoulder indicated at 780 cm^{-1} is assigned to Ti–OH bending vibrations and the broadness indicates a multiplicity of the surface OH species. The weak transitions at 195 and 162 cm^{-1} are probably due to OH- - -O stretching vibrations of surface species and might arise for example from linkages of the type:



(a) (b)

ACKNOWLEDGMENTS

The authors thank Professor A. C. Zettlemoyer for his interest in the work.

REFERENCES

1. Kruyt, H. R., and van Selms, *Rec. Trav. Chim.* **62**, 407 (1943).
2. Chessick, J. J., Zettlemoyer, A. C., and Young, G. J., *J. Colloid Sci.* **4**, 372 (1958).
3. Rao, K. S., *J. Phys. Chem.* **45**, 500 (1941).
4. Huttig, G. F., and Kosterhon, K., *Kolloid Z.* **89**, 202 (1939).
5. Ganichenko, L. C., Kieselev, V. F., Murina, V. V., *Dokl. Akad. Nauk USSR* **138**, 608–611 (1961).
6. Zettlemoyer, A. C., Iyengar, R. D., and Scheidt, P., *J. Colloid Interface Sci.* **22**, 172–8 (1966).
7. Egorov, M. M., Egorova, T. S., Krosil'nikov, K., *Zh. Fiz. Khim.* **32**, 2624 (1958).
8. Boutin, H., Prask, H., and Iyengar, R. D., *Advan. Colloid Interface Sci.*, in press. Elsevier, Amsterdam.
9. Hughes, D. J., Palevsky, H., Kley, W., and Tunkelo, E., *Phys. Rev.* **119**, 872, (1960).
10. Boutin, H., and Prask, H. *Surface Sci.* **2**, 261 (1964).
11. Lewis, K. E., and Parfitt, G. D., *Trans. Faraday Soc.* **62**, 204 (1966).
12. Yates, D. J. C., *J. Phys. Chem.* **65**, 746 (1961).
13. Iyengar, R. D., and Zettlemoyer, A. C., unpublished data.
14. Czanderna, A. W., and Honig, J. M., *J. Phys. Chem.* **63**, 620 (1959).
15. Liebisch, T., and Rubens, H., *Preuss. Acad. Wiss., Berlin* **8**, 211 (1921).
16. A. von Hippel, Kalnajs, J., and Westphal, W. H., *J. Phys. Chem. Solids* **23**, 779 (1962).
17. Narayanan, P. S., *Proc. Indian Acad. Sci.* **A32**, 279 (1950).
18. Ehrlich, P., *Z. Electrochem.* **45**, 362 (1939).
19. Assayag, P., Dode, M., and Faivre, R. *Compt. Rend.* **240**, 1212 (1955).

H. Boutin*,†
H. Prask*
R. D. Iyengar

Picatinny Arsenal
Dover, New Jersey
and
Center for Surface and Coatings Research
Lehigh University
Bethlehem, Pennsylvania
Received August 15, 1967;
revised September 25, 1967

---

*Guests at Army Materials and Mechanics Research Center, Watertown, Massachusetts.

†Present Address: Research Laboratory Division, Bendix Corp., Southfield, Michigan.