

expect a greater change in acid strength distribution than is observed on hydrating an M-46 catalyst. While a detailed discussion is beyond the scope of this paper, acidity measurements suggest that the acid centers on a cracking catalyst may differ in kind, rather than only in degree (of strength), and hence at least a significant and catalytically important fraction of them may be protonic acids, as indicated by the recent work of Holm, Bailey, and Clark (7). Other experiments tending to give additional support to this conclusion are in progress and will be discussed in a subsequent paper.

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Preparation and Surface Properties of Porous Titania

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THE PREPARATION OF TITANIA by simple hydrolysis of various titanium salts has been described numerous times in the literature. However, the heat stability of pure hydrous titania, as measured by surface area and pore volume, has not been adequately described. This study was made to define better the heat stability of pure hydrous titanias and of titanias containing known amounts of extraneous metal oxides.

The crystalline form of TiO_2 obtained from the hydrolysis of Ti^{4+} salts is dependent on the particular salt used, the preparative techniques employed, and subsequent heat treatment. Thus, Schossberger (9) and Pamfilov and Ivancheva (7) show that hydrolysis of TiCl_4 in water or dilute ammonium hydroxide yields rutile, whereas $\text{TiO}(\text{SO}_4)$ gives anatase. Anatase is converted to rutile by calcining at high temperatures (750° to 1800° F.). The transition may be catalyzed (3, 5) by dry hydrogen chloride, or aqueous hydrobromic acid; boric acid inhibits the transition. Anatase is transformed to rutile at lower temperatures with chloride present; with sulfate higher temperatures are required. The transition is not sharply defined, but is time-temperature-dependent. Thienchi (10) found that on heating anatase at 900° F. for 30 minutes only a trace amount of rutile appeared, whereas after 1 hour the transition to rutile was essentially complete. The transfor-

mation of anatase to rutile is irreversible (8). Brookite, another crystalline form of TiO_2 , has been prepared in admixture with anatase by hydrolysis of ethyl titanate. It is also converted to rutile by heating at 1300° F. or higher (2, 6).

EXPERIMENTAL PROCEDURES

Materials. The *n*-butyl, *sec*-butyl, and isopropyl titanates (Titanium Pigment Corp.) were used without further purification. The TiCl_4 and $\text{TiO}(\text{SO}_4)$ were of the best grade commercially available.

Pure Titania. The hydrolyses were carried out in amounts of aqueous media sufficient to obtain from 2 to 10% TiO_2 solids concentration.

Alkyl titanates yielded gelatinous precipitates on hydrolysis in water, dilute ammonium hydroxide, and dilute (ca. 5%) acetic acid. These precipitates were filtered with suction and water-washed. Hydrolysis in 20 to 70% acetic acid gave sols which set to firm, transparent hydrogels when heated to 150° to 180° F.

Hydrolysis of TiCl_4 in dilute ammonium hydroxide gave a gelatinous precipitate. Treatment of a cold aqueous solution of TiCl_4 with excess ethylene oxide resulted in the formation of a firm hydrogel. On prolonged washing of the

hydrogel with water, incipient peptization occurred before all chloride was removed.

Only gelatinous precipitates were obtained by hydrolyzing $TiO(SO_4)$ solutions in acidic, neutral, and basic media. As initially isolated these products contained as much as 5% residual sulfate and were even more difficult to purify than the products from $TiCl_4$.

Stabilized Titania. Alumina- and silica-stabilized titanias were prepared by first adding the desired amounts of an anhydrous aluminum isoamylate solution or ethyl silicate to the alkyl titanate and then hydrolyzing the mixed solution in aqueous media. Gelatinous coprecipitates were obtained in neutral and in dilute acetic acid solution. Hydrolysis in 10 to 50% acetic acid gave a true hydrosol which set to a firm transparent hydrogel on heating to 150° to 170° F.

Titanias stabilized with a mixture of Cr_2O_3 , ZrO_2 , Fe_2O_3 , and $Sm_2O_3-Gd_2O_3$ (American Potash Co., approximately equal amounts of the two oxides) were prepared by first dissolving CrO_3 , $ZrO(NO_3)_2$, $Fe(NO_3)_3$, and $Sm_2O_3-Gd_2O_3$ in 50% acetic acid solution and then hydrolyzing the alkyl titanate therein. True hydrogels were formed in all cases. The stabilized titanias were purified, heat-treated, and evaluated in the same manner as the unstabilized products.

Determination of Physical Properties. Surface area and pore volume determinations were made by the BET nitrogen-adsorption method (1). The crystal patterns of the titanias were obtained by x-ray diffraction of powder samples using a General Electric Type XRD-3 x-ray spectrometer, and were compared with those determined in like manner for naturally occurring rutile, anatase, and brookite.

RESULTS AND CONCLUSIONS

The surface areas and pore volumes of pure titanias prepared by hydrolyzing isopropyl titanate in several aqueous media are given in Table I. The data show the effect of heat treatment on these properties.

Table I. Hydrolysis of Isopropyl Titanate in Acetic Acid Solutions

Heat Treatment		Per Cent Acid in Water					
		None		5		50	
Hr.	° F.	Sq. m. /g. ^a	Cc./g. ^b	Sq. m. /g.	Cc./g.	Sq. m. /g.	Cc./g.
16	250	299	0.34
6	550	191	0.23	280	0.30
16	850	92	0.20
16	1000	89	0.19	41	0.10	77	0.18
6	1200	37	0.21	23	0.06
4	1400	5	0.12

^a Surface area.

^b Pore volume.

Titanias prepared by these techniques had high surface areas, on the order of 300 sq. meters per gram, after drying at 250° to 400° F. On calcining at higher temperatures, surface area and pore volume decreased substantially. As with other hydrous oxides—e.g., silica gel and alumina—which lose surface on heating but reach a relatively stable time-temperature-surface area plateau relationship, titania heated at a prescribed temperature for prolonged times showed good surface area retention after a relatively rapid initial loss in surface. Surface areas of all pure titanias calcined for times sufficient to reach the plateau (2 hours or more) show a linear relationship between the per cent loss in surface area and the reciprocal of the calcination temperature in degrees Kelvin:

$$\% \text{ surface loss} = -7.94/T \times 10^4 + 176$$

The linear relationship was found to hold over the

temperature range of 550° to 1400° F. There is also a continuous change in the crystal forms of these materials as temperature is increased. Initially, the material from the hydrolysis has the anatase structure. Between 850° and 1200° F. increasing amounts of rutile appear. At 1400° F. conversion to rutile is essentially complete (Figure 1). Hydrolysis of alkyl titanates in water only at room temperature resulted in a titania which, by x-ray diffraction, was principally anatase but also displayed a number of lines which are in common with brookite. This is shown in Figure 2, which compares tracings of this material with those for acid-hydrolyzed alkyl titanate (anatase) and the mineral brookite. The brookite diffraction lines appeared when it was hydrolyzed in water only and appeared independent of concentration or soaking period. Attempts to increase the brookite concentration by changing hydrolysis conditions, or to increase the heat stability of the surface by drying the hydrogel at room temperature in air and extracting the residual water with acetone, were unsuccessful.

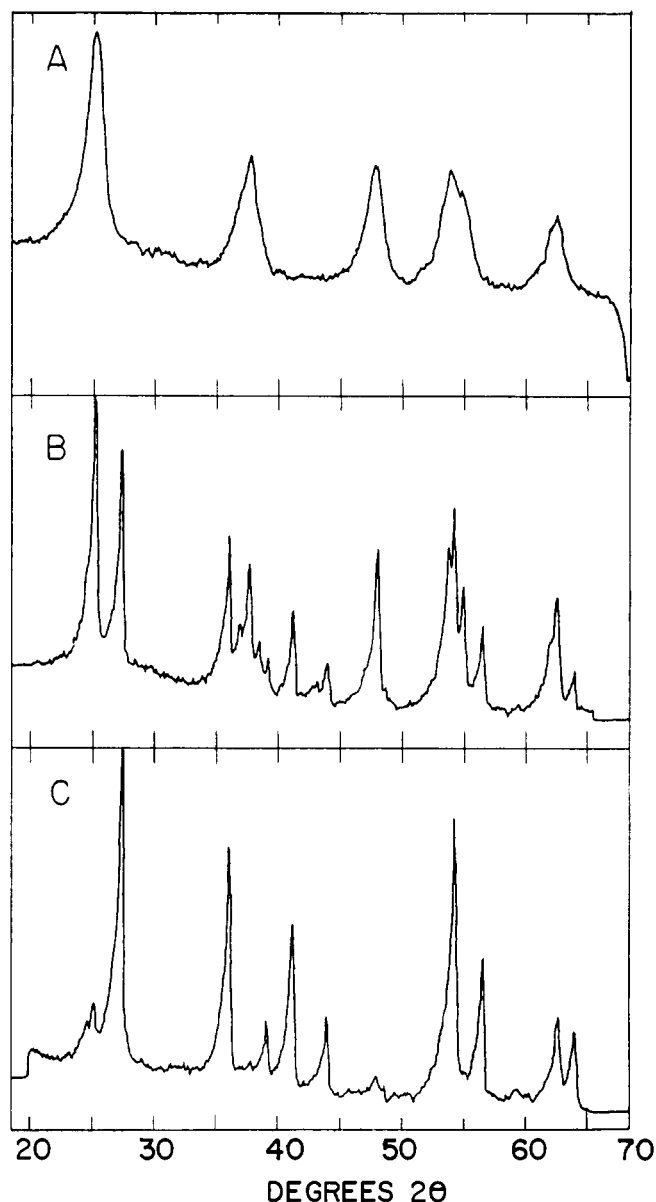


Figure 1. X-ray diffraction patterns for anatase and rutile preparations

A. Anatase, hydrous oxide calcined for 16 hours at 850° F.

B. Anatase plus rutile, hydrous oxide calcined for 6 hours at 1200° F.

C. Rutile, hydrous oxide calcined for 4 hours at 1400° F.

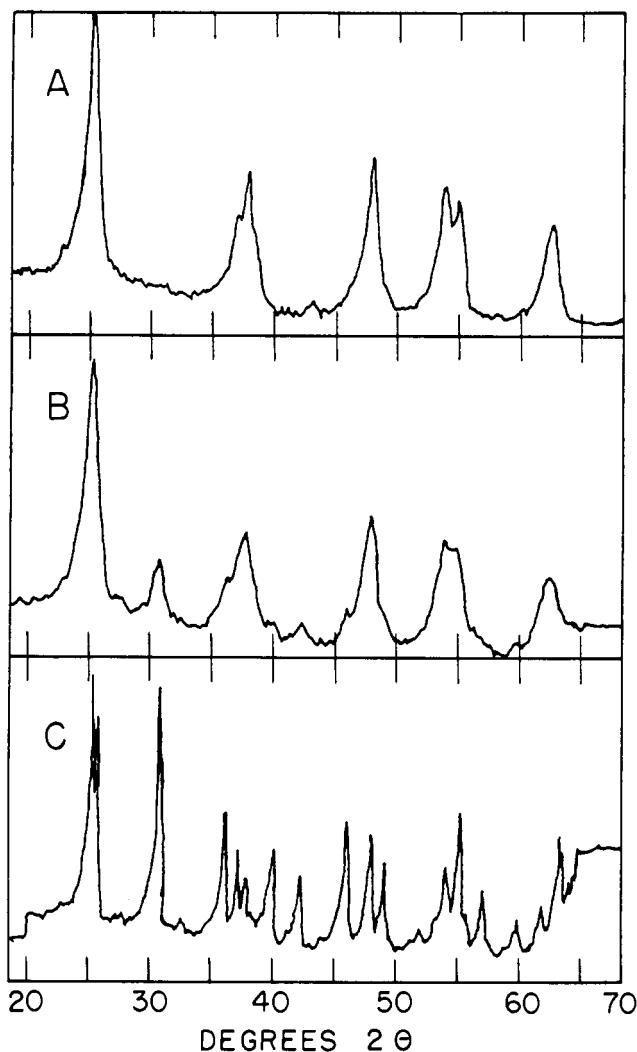


Figure 2. X-ray diffraction tracings for synthetic anatase-brookite mixture

- A. Anatase, prepared by hydrolyzing 1-propyl titanate in 5% acetic acid
 B. Anatase plus brookite, prepared by hydrolyzing 1-propyl titanate in water
 C. Mineral brookite

The effect of peptizing agents such as acetic acid on surface properties (Table I) is not well defined. The data show no advantage for making TiO_2 from a true hydrogel instead of a gelatinous precipitate. In a separate set of experiments, isopropyl titanate was hydrolyzed in water, dilute ammonium hydroxide, dilute nitric acid, and tartaric acid. In all cases comparable products were obtained. Other hydrolysis variables, such as sol concentration, hydrolysis temperature, and aging time also had negligible effect upon surface stability.

Isopropyl, *n*-butyl, and *sec*-butyl titanates when similarly hydrolyzed give comparable products. These materials have surface areas similar to that of TiO_2 prepared by hydrolysis of TiCl_4 . However, the TiO_2 from TiCl_4 was more easily converted from the anatase form to rutile than the titania from the alkyl titanates. This is believed due to the presence of free hydrochloric acid and/or chloride ions formed in the hydrolysis of TiCl_4 (3, 5). Bivalent anions, such as sulfate, act as stabilizers to the TiO_2 (4). Impure gels prepared by hydrolyzing $\text{TiO}(\text{SO}_4)$ contained as much as 5% residual sulfate. The surface area of this material after heating 16 hours at 100° F. was 180 sq. meters per gram. A portion of the same wet filter cake was washed (<0.1% SO_4) and calcined similarly. The surface area of the washed TiO_2 was 60 sq. meters per gram, which is very close to that of the pure titania prepared from alkyl titanates. Unlike the

sulfate, residual chloride imparts negligible stability to the surface.

The rapid degradation of pure titania with increasing temperature can be arrested by incorporating small amounts of other metal oxides with the TiO_2 . The stabilizing action of small amounts of silica and alumina on titania is shown in Table II. With the preparations comprising alumina, aluminum isoamylate was added to the alkyl titanate prior to hydrolysis; with silica, ethyl silicate was added. The hydrolysis medium was 50% acetic acid.

Addition of these stabilizers not only raises the level of the surface areas and pore volumes relative to unstabilized TiO_2 but also markedly reduces the rate of degradation by heat.

The stabilizing action of Cr_2O_3 , ZrO_2 , Fe_2O_3 , and Sm_2O_3 - Gd_2O_3 on titania was also investigated. These materials were prepared as described above. The surface properties and heat stabilities of the product are given in Table III.

Table II. Properties of Alumina- and Silica-Stabilized Titania

Composition, Wt. %	Heat Treatment			
	16 Hr. at 1000° F.		6 Hr. at 1200° F.	
	S. area	Pore vol.	S. area	Pore vol.
100 TiO_2	77	0.18	23	0.06
2 Al_2O_3 -98 TiO_2	106	0.21	69	0.17
5 Al_2O_3 -95 TiO_2	121	0.24	112	0.24
2 SiO_2 -98 TiO_2	120	0.32	110	0.28
5 SiO_2 -95 TiO_2	149	0.40	133	0.37

Table III. Surface Properties of Stabilized Titania

Composition, Wt. %	Heat Treatment			
	16 Hr. at 1000° F.		6 Hr. at 1200° F.	
	S. area	Pore vol.	S. area	Pore vol.
100 TiO_2	77	0.18	23	0.06
2 (Sm_2O_3 - Gd_2O_3)-98 TiO_2	115	0.33	103	0.33
2 Fe_2O_3 -98 TiO_2	76	0.20	70	0.16
10 ZrO_2 -90 TiO_2	104	0.21	91	0.22
10 Cr_2O_3 -90 TiO_2	75	0.22	44	0.20

The samarium-gadolinium oxide mixture is as good as silica and alumina as a stabilizer, whereas chromia, zirconia, and Fe_2O_3 are not as effective.

It can be concluded that the surface area of pure titania is unstable to heat and is degraded rapidly to low surface area materials at temperatures above about 500° F. Addition of a few per cent of SiO_2 , Al_2O_3 , or Sm_2O_3 - Gd_2O_3 to the TiO_2 exerts a stabilizing action toward surface area degradation by heat.

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