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Preparation and Properties of Active Thorium Oxide from Thorium Hydroxide

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The circumstances in the preparation of active thorium oxide which control the properties of the oxide have been investigated for thoria obtained by precipitation and thermal dehydration of the hydroxide. Surface area and crystallite size determinations, as well as some tests of catalytic activity, have been used to characterize the thoria. In addition to the temperature of conversion of the hydroxide to the oxide, the reagent concentrations, methods of mixing and extent of washing in the process of preparing the hydroxide have been found to affect strongly the nature of the resulting oxide. The dehydration of alcohols is found to be much more sensitive to the surface area of the catalyst than is the dehydrogenation.

INTRODUCTION

Active thorium oxide has been reported to be a catalyst for several types of reactions. Among these is the decomposition of alcohols, for which it serves as either a dehydration or dehydrogenation catalyst, depending in a complex way upon the procedure by which the oxide is prepared and also upon the conditions under which the reaction is carried out. Schwab (*1*) discussed the directive effects in this reaction in terms of the requirement that, for a concerted dehydration reaction, there be available two opposite walls of a pore or crack of suitable dimensions. It has also been reported recently that thoria catalyzes the dehydration of 2-ols to form selectively 1-olefins (*2*).

A study of the relation between the structure of thorium oxide and the nature of the reactions which are catalyzed at its surface has been underway in these laboratories. This paper presents the results of work dealing with the effects of conditions of preparation of the oxide, as derived from precipitated thorium hydroxide, on the physical properties of the catalyst, with some consideration of the relation to catalytic activity. Subsequent papers will treat the course and mechanism of reactions catalyzed by the thoria surface.

METHODS

The general procedure for the preparation of thorium oxide employed in this work has been the precipitation of thorium hydroxide from a solution of thorium nitrate by addition of ammonia, filtering, washing, and drying the precipitate, and activation by heating at a suitable elevated temperature between 400° and 800°C. Both the conditions of precipitation of the hydroxide and the conditions of conversion of the hydroxide to the oxide affect the properties of the final product. To study the precipitation and washing process, a standard activation procedure was followed, which is implied for all materials in the following discussion unless other activation conditions are specifically described. In this procedure, the filtered and washed hydroxide was dried for approximately 24 hr at 110–120° and was then heated under vacuum for 4 hr at 600°C.

The thorium nitrate used in preparing the catalyst samples was the tetrahydrate, as obtained from Fisher Scientific Company. The ammonia was Baker and Adamson, reagent grade, containing approximately 29% NH_3, used as received. For almost all the catalysts described here, the ammonia was taken from a single bottle.

The surface area of each oxide sample was calculated from data on the adsorption of nitrogen at liquid nitrogen temperature, obtained in a conventional volumetric apparatus, by application of the BET isotherm equation. Before determination of the isotherm, the sample was cleaned by evacuation at 200° for 1 hr. Average size of the crystallites composing the solid was estimated from the width of X-ray diffraction lines obtained with a Norelco recording diffractometer. Copper K_α radiation was used, with a nickel filter. The samples were ground to —400 mesh and spread in a shallow holder. Crystallite size was estimated by the Scherrer equation (*3*),

$$L = K\lambda/\beta \cos \theta$$

in which L is the average crystallite dimension perpendicular to the set of planes producing diffraction, K is a constant assumed equal to unity, and $B = B_1^2 - b^2$, where B_1 is the measured half-width at half-maximum intensity and b is the corresponding value for crystalline ThO_2.

RESULTS AND DISCUSSION

Factors in Hydroxide Preparation Affecting the Surface Area

Two of the qualitative circumstances surrounding the formation of the hydroxide from which the oxide is derived were found to be quite important. The first of these is the rate at which ammonia is added to the solution of thorium nitrate. Under the conditions used in this work, large surface area is developed only if the ammonia is poured rapidly into the solution. Although the points given in Table 1 suffer from lack of reproducibility because of the method of washing, they indicate that, when ammonia is run in slowly from a buret, the surface area is uniformly quite low. A number of other precipitations have been carried out, under various conditions; in no case did the surface areas for slow precipitation exceed the order of those given in Table 1, while oxides of much larger area could be obtained, as will be shown below, by use of rapid precipitation. Unless otherwise specified, the materials described in this paper were made by the rapid precipitation process.

TABLE 1

SURFACE AREAS OF THORIUM OXIDE[a] SHOWING EFFECTS OF RATE OF ADDITION OF AMMONIA AND OF AMOUNT OF WASHING

Time to add ammonia (min)	Volume of wash water (ml)	Final pH of washings	Surface area of oxide (m^2/g)
0	300	9	1.1
0	700	7	4.7
0	900	5	6.1
1.6	300	9	1.4
1.3	900	7	1.0
1.6	800	5	9.4
1.9	900	5	4.8
10.9	300	9	0.7
9.3	900	7	1.3
9.6	1050	5	5.2
35.0	300	9	0.4
35.5	800	7	0.7
36.5	900	5	0.7
69.0	300	9	0.0
66.9	800	7	0.5
74.9	1100	5	0.3

[a] Fifty ml of concentrated ammonia was added to 500 ml of solution containing 40 g $Th(NO_3)_4 \cdot 4H_2O$. The precipitate was washed on the filter with sufficient water to give the indicated final pH of the wash.

The data given in Table 1 were obtained for samples in which the hydroxide precipitate was washed with water as it remained in the form of filter cake on filter paper in a Büchner funnel or on a fritted disc. The sixth and seventh entries of the table are included particularly to illustrate the fact that the reproducibility of the areas of the oxides prepared in this way was rather poor. When washing was carried out by slurrying the hydroxide with wash water, stirring with a mechanical stirrer, and decanting the supernatant liquid, the condition of the resulting oxide was found to be quite reproducible. Most of the results described below were obtained by this method of washing, which thus becomes the second important feature of hydroxide preparation.

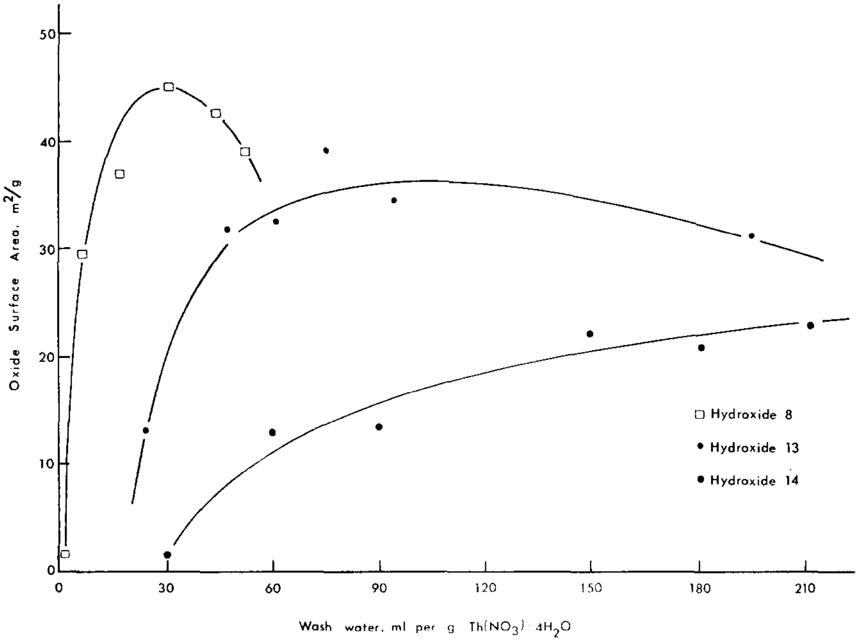

FIG. 1. Effect of volume of water used in washing thorium hydroxide on the surface area of the resulting oxide, for three different hydroxide samples.

Table 1 also indicates an increase in area with larger volumes of wash water. The results shown in Fig. 1, obtained by the more satisfactory washing method, show clearly the effect of the amount of washing on the surface area of the product oxide. Hydroxide 8 was prepared from a solution containing 40 g $Th(NO_3)_4 \cdot 4H_2O$ in 500 ml (0.145 *M*) by addition of 50 ml of concentrated ammonia. The filtered precipitate was divided into six equal portions, each of which was washed with a different amount of water by the process of slurrying, stirring, and decanting. As will be seen later, the thorium nitrate concentration was below the optimum value for developing maximum surface area of the oxide. Hydroxide 13 was prepared and washed in the same way; the only difference was that the initial precipitation was carried out by adding 60 ml of concentrated ammonia to a solution of 50 g of hydrate in 340 ml of water (0.27 *M*). With hydroxide 14, an attempt was made to determine the effect of amount of wash water used by taking samples as washing proceeded, rather than by working with individual portions of the precipitate. Following the initial precipitation by addition of 200 ml of ammonia to 80 g of the hydrate in 350 ml of aqueous solution (0.41 *M*), all of the filtered precipitate was slurried in 300 ml water and the slurry was stirred mechanically for 10 min. A portion of the suspension was removed during the stirring, and the precipitate in this portion was separated by filtration, dried, and activated. The wash water was decanted from the remaining material and 400 ml of fresh water was added. After another period of stirring for 10 min, a second sample was removed. This process was repeated and samples were taken after each washing with 400 ml of water. The beginning of peptization was observed to occur after a total wash volume of 1500 ml, and the wash water had a pH of 7 at a total volume of 1900 ml.

All three sets of data show a rapid rise of surface area during the early washing stages, followed by a maximum value beyond which there is a plateau or a slow decline with further washing. During this process, the pH of the wash water drops from 9 to 5 and the concentration of nitrate ion in the wash water undergoes a simultaneous decrease. The maximum in the surface area is reached when washing is continued to a pH slightly greater than 7. It is also quite interesting to notice that a material for which the maximum surface is higher requires a smaller amount of washing to develop this maximum value of the surface. This indicates a more open structure of the hydroxide precipitate, permitting freer access of the wash water to the interior of the particles with consequent easier removal of the excess ions. To determine the effect of concentration of the thorium nitrate solution on properties of the precipitate, aliquots of 1.80 *M* and 0.30 *M* solutions, each aliquot containing the equivalent of 6.0 g of the thorium nitrate hydrate, were diluted to various concentrations and 10 ml of concentrated ammonia was added rapidly to each. The results are shown in Fig. 2, with the oxide surface area plotted against the logarithm of the thorium ion concentration. It is observed that a maximum area is obtained, under these conditions, for a concentration near 0.3 *M* with areas decreasing rapidly below 0.1 or above 1.0 *M* concentration.

The effect of varying the ratio of ammonia to thorium ion concentration was studied for solutions containing 80 g $Th(NO_3)_4 \cdot 4H_2O$ per liter. As shown in Table 2, the areas rise rapidly with concentration of ammonia at the lower values and then level off, with further excess of

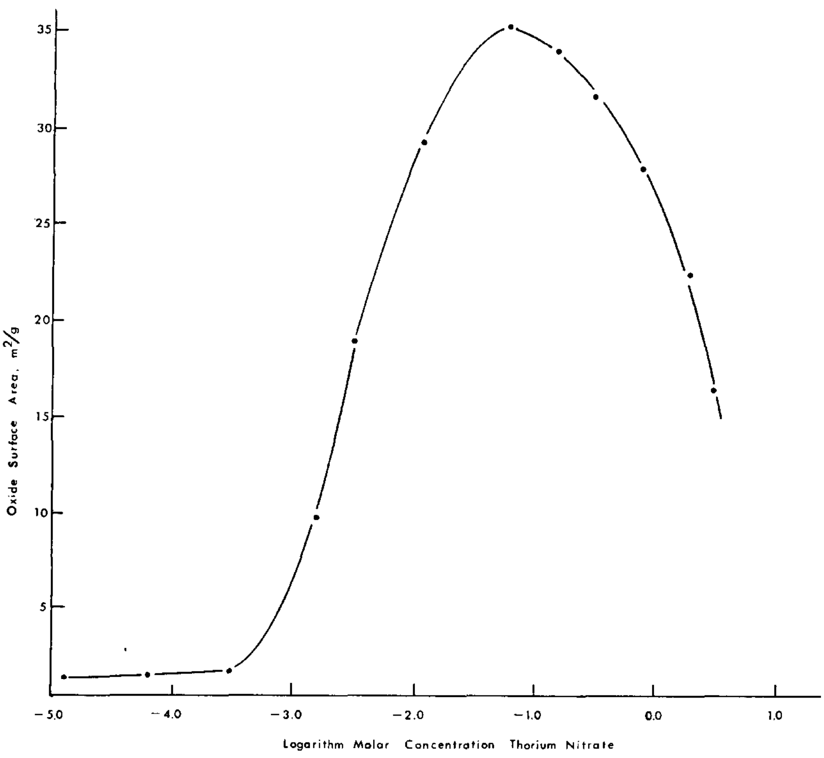

FIG. 2. Effect of concentration of thorium nitrate on the surface area of the resulting thorium oxide.

TABLE 2
SURFACE AREAS OF THORIUM OXIDE SHOWING EFFECT OF AMOUNT OF AMMONIA ADDED IN PRECIPITATION

Volume ammonia added [ml per 100 ml $Th(NO_3)_4$ solution]	Volume wash water (ml)	Surface area of oxide (m^2/g)
5	1200	8.3
7	1200	24.4
10	1600	31.2
15	1600	39.4
20	1600	38.2
30	2800	41.2
50	3000	37.6
100	3000	41.7

ammonia having little effect, provided, of course, that washing of the precipitate is sufficient to remove excess ions. The stoichiometric amount of ammonia is slightly above 4 ml; no persistent precipitate is formed below this concentration. The data show also that several times the stoichiometric amount is required, at least at the concentration of thorium nitrate used here, to produce the maximum surface area of the oxide.

Factors in the Activation Process Affecting the Surface Area

The effects of temperature and atmosphere of activation are indicated in Fig. 3. The hydroxide used for this experiment was precipitated as a single large batch. To a liter of solution containing 166 g $Th(NO_3)_4 \cdot 4H_2O$ (0.30 M) there was added rapidly 200 ml of ammonia. The precipitate was filtered off and washed as a slurry with mechanical stirring. Various portions of the dried material were heated for 4 hr, either (1) under vacuum in a Vycor tube, or (2) in a Vycor boat exposed to the air, or (3) in a Vycor tube in a stream of water vapor generated in a boiler and

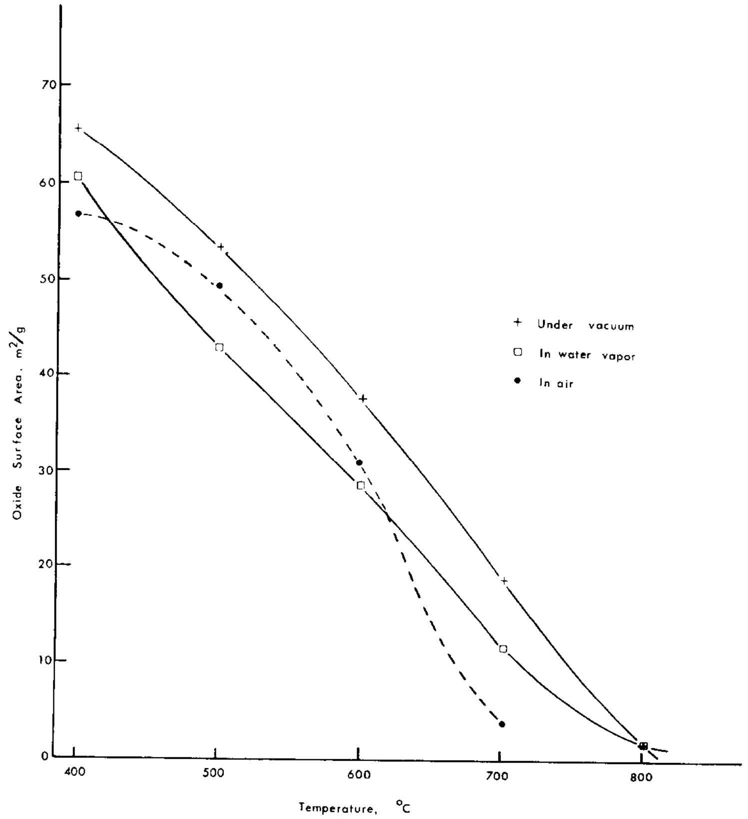

FIG. 3. Effect of activation conditions on oxide surface area.

heated in a preheating furnace ahead of the activation furnace. Exposure to water vapor or to the atmosphere is seen to reduce the area somewhat, with the effect of the atmosphere being greatest at 700° and the effect of water vapor greatest at 500° and 600°. However, there is not a drastic difference produced by activation atmosphere.

The time of heating of the material during the preparation of the oxide also affects the oxide surface area. As would be expected, a longer time of heating causes the surface area to be smaller. Portions of one particular sample were heated at 600° in vacuum, surface areas were determined, and then heating was resumed. This was repeated several times and results of two of these runs are shown in Fig. 4. The hydroxide used in this experiment was made by adding rapidly 100 ml of ammonia to a liter of solution containing 80 g of the hydrate and washing the precipitate by slurrying and decantation.

Crystallite Size of the Oxide

The estimates of average size of the crystallites are based upon the broadening of X-ray diffraction lines observed when the region over which perfect crystallinity extends is less than perhaps 500 Å in thickness. Measurements were made on the 111 diffraction line, which is the most prominent in the pattern of the cubic ThO_2 lattice. On several samples, widths were also measured for the 220 and 311 lines, which have moderate intensity. The accuracy of measurement of the width for the less intense lines was also less, causing greater scatter of points, but no systematic change of the relative widths of the three lines could be observed in a variety of samples. Figure 5 shows crystallite size data for the

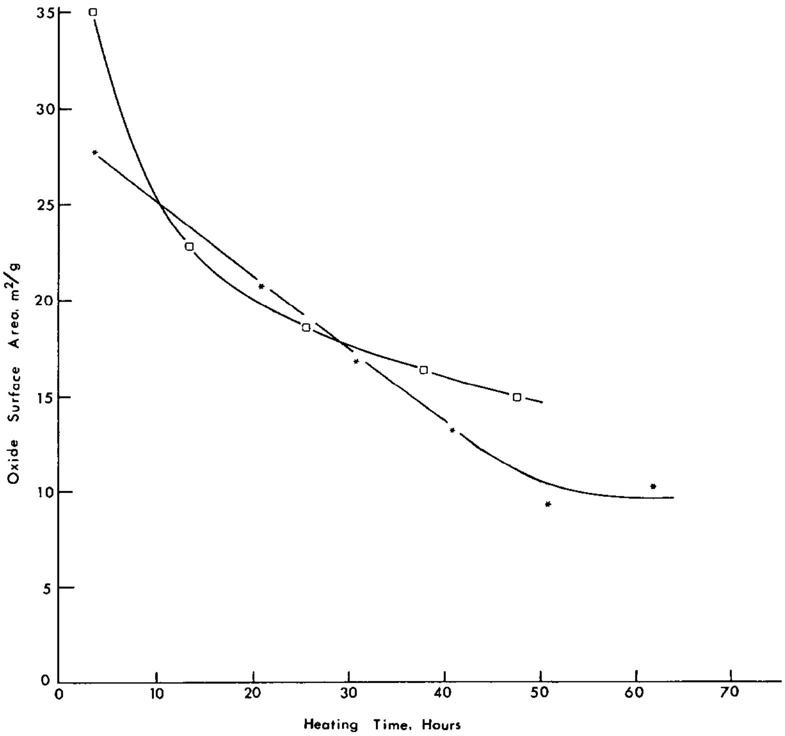

FIG. 4. Effect of heating time on oxide surface area. Curves are for two samples having different initial areas.

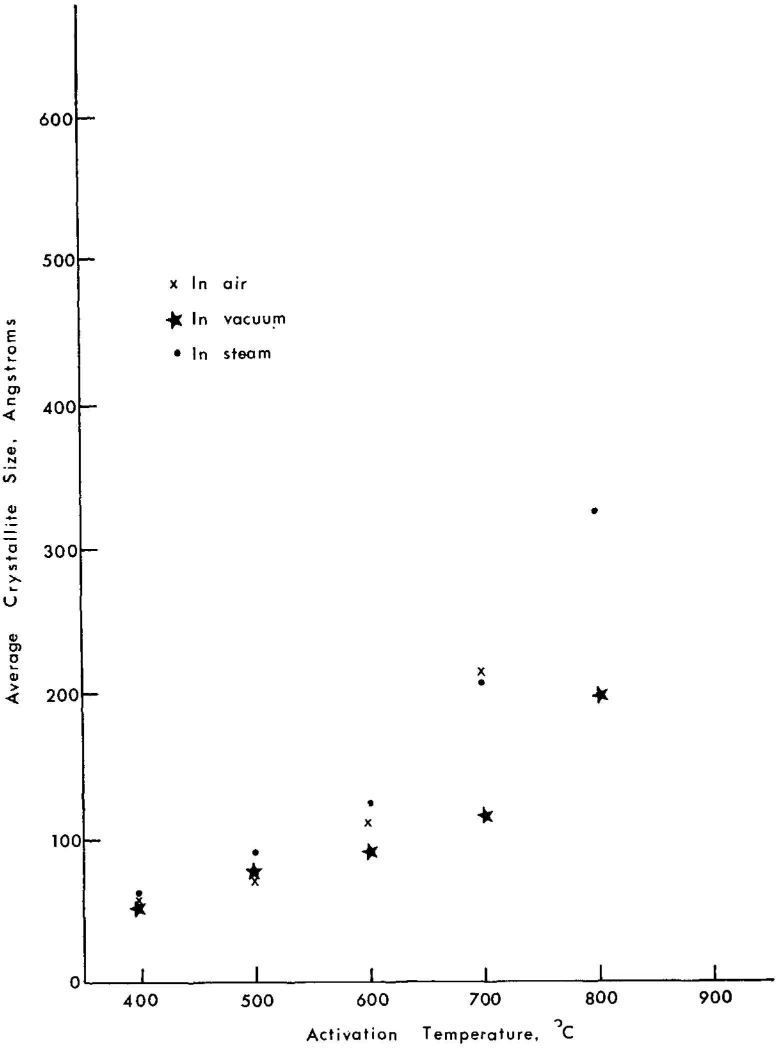

FIG. 5. Effect of activation conditions on crystallite size of thorium oxide from hydroxide 12.

same samples, designated hydroxide 12, for which surface areas were given in Fig. 3.

Another series of samples, designated hydroxide S, each prepared by a separate precipitation rather than taken as portions of a common batch, was activated at various temperatures. Portions were heated 3 hr in a vacuum, heated 5 hr in a vacuum, heated 5 hr in a vacuum and then used for periods of 12 to 100 hr as alcohol decomposition catalysts, or heated 3 hr in water vapor. To obtain each sample, 50 ml of ammonia was added to a solution of 42.5 g of hydrate in 250 ml of water, and the filter cake was washed in the funnel until the wash was negative to pink litmus and then with 500 ml of additional water. The results are shown in Table 3 and the crystallite size plotted against surface area in Fig. 6. A third series, designated hydroxide VI, was obtained by activation of a precipitate obtained by adding 250 ml of ammonia to 1250 ml of solution containing 210 g of hydrate, and filtering and washing in the funnel. The results are also shown in Table 3 and Fig. 6.

TABLE 3
AVERAGE CRYSTALLITE SIZE (ÅNGSTROMS) FOR THORIUM OXIDE CATALYSTS

Activation temp. (°C)	Hydroxide S				Hydroxide VI
	After 3 hr in vacuum	After 5 hr in vacuum	After 5 hr and use as catalyst	After 3 hr in steam	After use as catalyst
400	44	—	54	47	—
500	58	74	75	67	80
600	76	89	92	98	115
700	103	114	116	—	162
800	162	210	211	180	274

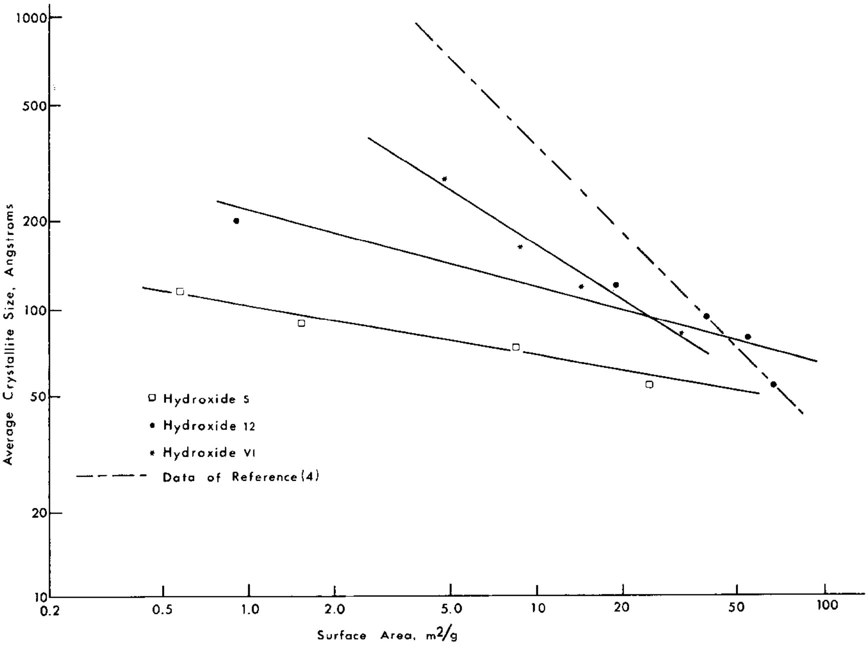

FIG. 6. Relationship between crystallite size and surface area for thorium oxide.

Consideration of all the data on crystallite size indicates that the numerical value is primarily related to the temperature of activation rather than to any circumstance of precipitation of the hydroxide. Of 95 samples activated by the usual procedure of heating in vacuum for 4 hr at 600°, 79 had sizes within the range 80–100 Å. For any given conditions of such precipitation, there is a reasonably linear relationship on a log–log plot between surface area and average crystallite size. Examples are shown in Fig. 6, along with the line found by Allred, Buxton, and McBride (*4*) for ThO_2 from the oxalate. The sintering process appears to occur in parallel fashion on various samples, leading to a decrease in surface area and an increase in crystallite size. However, the magnitude of the surface area obtained is essentially unrelated to the crystallite size. One must conclude, therefore, that it is related to the extent of aggregation of the primary structural units which occurs during the precipitation process.

Catalytic Activity of the Oxide

Although this paper does not deal primarily with the reactions catalyzed by thoria, some of the results obtained for alcohol decomposition will be briefly discussed. For the study of this reaction a microcatalytic reactor was employed, in which a small portion of ethanol was vaporized into a stream of helium and passed over a bed of the oxide catalyst, maintained at a temperature between 275° and 400°C. The condensable products of the reaction were trapped out and then analyzed by vapor phase chromatography. In general, both dehydrogenation and dehydration were observed. No ether was found in the products of the reaction over any catalyst. The amount of alcohol reacted was accounted for, within 2–3%, by the products formed in the two reactions, dehydration to ethylene and water, and dehydrogenation to hydrogen and acetaldehyde. The three condensable products were determined directly, and the amount of hydrogen was taken as equivalent to the acetaldehyde found.

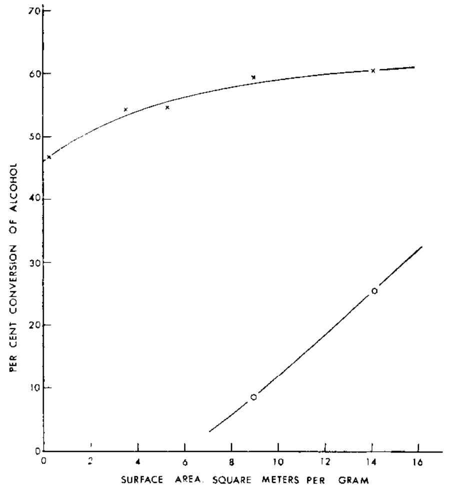

FIG. 7. Relation of catalytic activity in decomposition of ethyl alcohol to surface area of thorium oxide. The catalysts were activated at 600°C and pelleted at 90 000 psi. The reaction temperature was 350°. Crosses represent per cent of the alcohol feed converted to acetaldehyde and hydrogen; circles represent per cent of the alcohol feed converted to water and ethylene.

With catalysts having areas as low as 1 m^2/g, extensive dehydrogenation occurred, while dehydration was only observed with oxide samples having relatively large surface areas. Figure 7 shows typical conversions of ethanol samples to acetaldehyde and to water for various thorium oxide catalysts. The data given here are for the reaction run at 350° under uniform conditions for all samples. All catalysts used in obtaining the data in this plot were prepared by adding excess ammonium hydroxide to thorium nitrate solution, filtering off the resulting precipitate, washing the precipitate in the filter funnel until the washings were neutral to litmus, drying at 110°, and heating in vacuum at 600° for 4 hr. The material was then powdered and formed into pellets at 90 000 psi. The differences in area were the result of changing the rate of addition of the ammonia and the concentration of the thorium nitrate in the precipitation step.

The three samples of low area produced no detectable dehydration of the alcohol, while the two of higher area did produce considerable dehydration. These results may be explained if one associates the dehydration reaction with interior surfaces or pore walls of the oxide, which are not present in the low-area materials.

ACKNOWLEDGMENTS

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