

PREPARATION AND ADSORPTIVE PROPERTIES OF THORIUM OXIDE

By

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A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

June, 1965

ACKNOWLEDGMENTS

The assistance of the author's committee chairman, Dr. Wallace S. Brey, Jr., in completing the work reported here is gratefully acknowledged. Even more appreciated, however, has been his influence on the author's over-all outlook.

The author would like to acknowledge the financial support received from the Atomic Energy Commission during the course of this investigation.

Thanks are also extended to Mrs. Thyra Johnston for typing the manuscript.

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CHAPTER I

INTRODUCTION

The nature of heterogeneous catalysis is such that the investigation of this topic lends itself to two general methods of attack; one is the study of the reaction course by measurement of its kinetics, products produced, relative amounts of products produced, radio-isotope distribution in products from labeled reactants, etc., while the other approach is to study the nature of the catalytic material itself in order to elucidate the structure of the catalytic surface.

Numerous studies have been made employing the study of the reaction and these studies have shed considerable light on the reaction path. However for a material to serve as a catalytic material it is necessary for the reactant to be in contact with the catalytic material at some stage of the reaction. Thus any complete description of the reaction path must present the "structure" of the reactant-catalyst species. This then requires a knowledge of the structure of the catalytic surface.

The structure of the catalytic material is determined to a great extent or even completely by the preparation and pretreatment of the catalytic material. Yet one encounters

all too frequently in the literature detailed studies of catalytic reactions using a catalyst prepared by "the thermal decomposition of the metallic salt" or "a sample of thoria of ordinary reagent grade and unknown history." This last quote appeared in the literature in 1950 so meager description of catalytic material is not restricted to the pioneering studies.

Thorium oxide has been widely studied as a dehydration-dehydrogenation catalyst for alcohols since the pioneering work of Sabatier and Maihle (1). This catalyst has been found to give dehydration almost exclusively by some investigators (1) while others have found the catalyst to produce both dehydration and dehydrogenation, the amount of each reaction depending on the particular thoria catalyst used (2). In addition to the dehydration-dehydrogenation properties, a recent investigation by Legg (3) has shown that this catalyst is able to cause condensation of some n-alcohols to yield either a symmetrical secondary alcohol or ketone. Many of the catalysts which yielded the above contradictory results were prepared by "the same method."

The present investigation was undertaken to study the effect of the various parameters of the thoria catalyst preparation by noting the effect of a given parameter on some physical property of the catalyst. Certainly one physical property which would be related in some manner to

catalytic activity of a material is the surface area. Thus the effect of various parameters of the preparation was determined by a measurement of the surface area by the B.E.T. method (4) using nitrogen at its boiling point as the adsorbent. This method for surface area measurements is not without criticism, some of which will be discussed in more detail in Chapter V; however it has given very reproducible results when employed by different workers and is much more convenient and rapid than measuring the catalytic activity itself.

Lawson (5) obtained n.m.r. results for materials adsorbed on thoria which appeared to depend upon the catalyst preparation. Thus another area of the present study was to be an n.m.r. study of water adsorbed on thoria samples whose method of preparation led to reproducible nitrogen surface areas. In this study it is desirable to be able to obtain the water surface coverage without resorting to an assumption as to the area occupied by a water molecule since this area may vary for different samples (6). Therefore measurement of surface areas for several catalysts was done to obtain the amount of water for a monolayer coverage independent of the nitrogen surface area.

CHAPTER II

LITERATURE REVIEW

A. Thoria Preparation Methods Described for Catalytic Reaction Studies

The preparation of catalytic materials was reviewed by Ciapetta and Plank (7) and by Griffith and Marsh (8); in addition the latter authors give a general discussion of catalyst evaluation. The literature contains thousands of recipes for specific catalyst preparations and numerous new ones appear in the literature each year. Catalyst preparation directions are usually given, more or less completely, in the literature for catalytic reaction studies. Unfortunately these descriptions are very incomplete for thoria. Most of the preparation procedures given for thoria preparation merely state that the catalyst was prepared by thermal decomposition of a thorium salt or precipitation from a dilute solution. Very few of the descriptions are given in sufficient detail so that a similar material could be prepared with any degree of confidence; hence these preparative methods will not be discussed here.

One reaction study which presents a detailed description of a thoria preparation is that of Kistler, Swann, and Appel (9). These authors prepared thorium

hydroxide from the nitrate by precipitation with excess ammonia, washed free of electrolytes, and then peptized the hydroxide at 90°C by the addition of thorium nitrate. They obtained a yellow-orange sol. They dialyzed this sol and then concentrated it by vacuum evaporation. They then added sufficient citric acid to cause gel formation on standing; the amount needed was learned from past experience. The gel was first washed with acetone, then with methanol. Then the gel was heated in an autoclave nearly filled with methanol to a point above the critical temperature of the alcohol. After the critical temperature was reached the alcohol was slowly bled from the autoclave. This catalyst was more active for the formation of ketones from acids than three other catalysts; however the descriptions of the preparation procedures for the comparison thoria catalysts were very meager.

Later Kearby and Swann (10) used a variation of the preceding catalyst preparation but found this catalyst to be much less active for the dehydration-dehydrogenation of ethyl alcohol than the one described in the last paragraph.

Dissertations by Legg (3), Moreland (11), and Schmidt (12) contain discussions of various thoria catalyst preparations used for the dehydration-dehydrogenation of alcohols which had appeared in the literature. In addition Moreland studied the effect of catalyst preparation by the

precipitation method on the dehydration-dehydrogenation of ethanol in a batch reactor.

The use of thorium oxide as a breeder fuel in nuclear reactors has motivated numerous studies concerning the preparation of thorium oxide. However the goal of these studies was the preparation of high density thoria instead of high surface area thoria; hence this area of preparation studies will not be considered here.

B. Preparation of Thoria from Thorium Oxalate

There have been several studies of the thermal decomposition of thorium oxalate hydrate but few of these studies have been directed toward the examination of the thoria which results from the decomposition.

Beckett and Winfield (13) employed thermograms and electrical conductivity to study the decomposition of thorium oxalate hexahydrate. They found that ThO_2 may appear at temperatures as low as 200°C . Thorium carbonate concentration reached a maximum at approximately 300°C and was only 0.075 mole/mole of thorium oxide. By chemical analysis they found that only the dihydrate was present at 180°C . Between 180 and 290°C not only water but also CO and CO_2 was lost. Extensive decomposition of the oxalate began at 295°C and was practically isothermal. When the oxalate decomposition was complete there was still about one-half mole of water remaining in the thoria.

Winfield (14) in an earlier study found that a thoria catalyst active for the dehydration of 2,3-butanediol was obtained by the thermal decomposition of thorium oxalate prepared from thorium nitrate only if the thorium oxalate had been washed sufficiently to remove traces of the nitrate ion. In this publication the author also reported that the thoria from the thermal decomposition of the oxalate was a much more active catalyst than the ones prepared by ignition of the thorium nitrate or by ignition of "hydroxide" precipitated from a salt solution; indeed these latter two preparations gave very inactive catalysts.

Winfield (15) also found that thoria prepared from washed thorium oxalate by ignition at 400°C for six hours had a B.E.T. surface area of $24.3 \text{ m}^2/\text{g}$ when measured using nitrogen at liquid oxygen temperature. From water adsorption isotherms, using a value of $\sigma = 10.6 \text{ \AA}^2$ for water, the author calculated a surface area of $56 \text{ m}^2/\text{g}$ for this same catalyst.

D'Eye and Sellman (16) thermally decomposed thorium oxalate dihydrate in an air atmosphere. They found that the anhydrous oxalate is formed by heating to a temperature of 270°C. At 320°C they found CO and CO₂ to be liberated in a ratio slightly greater than unity; after five hours at 320°C they increased the temperature to 420°C and the ratio CO:CO₂ decreased to approximately 0.3. The total mass of CO

and CO_2 exceeded theory; they proposed disproportionation of CO to C and CO_2 followed by air oxidation of the C at 420°C to CO_2 .

Padmanabhan, Saraiya and Sundaram (17) performed a differential thermal analysis (D.T.A.) on thorium oxalate dihydrate. They obtained endothermic peaks at approximately 160° and 270°C which they attributed to successive loss of the water of hydration. They obtained an exothermic peak at roughly 390°C . Wendlandt, George, and Horton (18) performed the same experiment with thorium oxalate hexahydrate. They also obtained the first two endothermic peaks and attributed these to the initial loss of four molecules of water of hydration, followed by the loss of two more molecules of water of hydration. However these authors obtained an endothermic peak at 385°C and a broad exothermic peak at about 560°C .

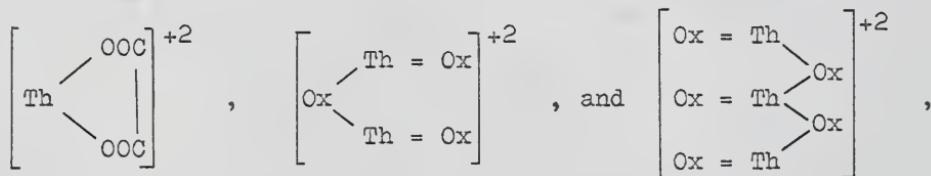
Claudel, Perrin, and Trambouze (19) have explained the above D.T.A. results as being due to the experimental conditions. With a sample packed tightly in the sample holder they obtained three endothermic peaks at 152° , 300° , and 379°C . They interpreted these peaks to correspond to the removal of four molecules of water, one molecule of water, and removal of the last molecule of water of hydration simultaneously with the decomposition of the thorium oxalate, respectively. However, when they did not pack the sample

tightly and passed a current of air through the sample during decomposition they obtained not only an endothermic peak at 364° but also an exothermic peak at 426°C. They attributed the three endothermic peaks to the actual decomposition of the thorium oxalate hexahydrate and the exothermic peak to catalytic oxidation of carbon monoxide which is an exothermic reaction.

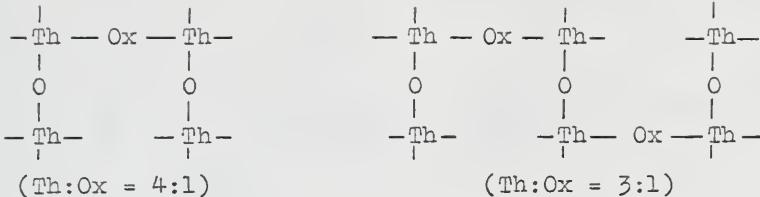
Claudel et al. (20) followed the thermal decomposition of the hydrates of thorium nitrate and oxalate by the simultaneous thermograviometric, D.T.A., and emanation methods. They concluded that thorium nitrate decomposed by successive loss of a water of hydration and then decomposition of the thorium nitrate. They found the decomposition reaction of anhydrous thorium oxalate to be a complex reaction. The D.T.A. curve has two peaks which they attributed to the formation of two- or three-dimensional structures through an intermediate $\text{Th}(\text{CO}_3)_2$ phase. The curve for the emanation has two peaks corresponding to those for the D.T.A.; in addition it has a peak for the initial thorium oxalate decomposition.

Bobtelsky and Ben-Bassat (21) studied the titration and precipitation of thorium as the oxalate from a solution of the nitrate. They observed that precipitation did not occur until the ratio Th:Ox (Ox represents oxalate anion) was unity. Further addition of oxalate induced bonding

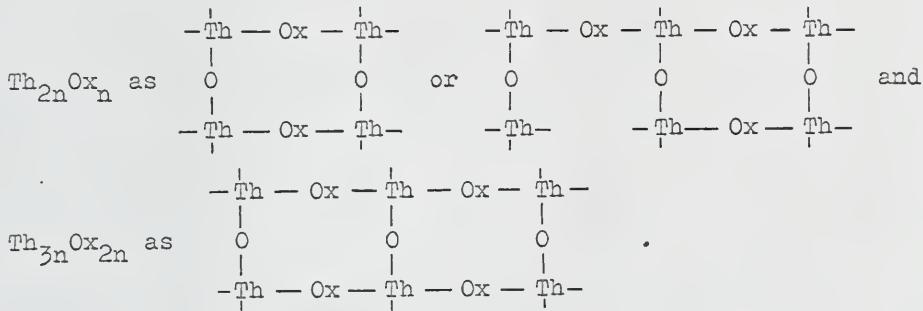
between the soluble thorium-oxalate complexes, or bonding of the soluble oxalate complex with oxalate ions or with other anions in the solution and the formation of cyclic compounds which are insoluble. In acid solutions, that is, pH less than ca. 5, the authors supposed the simple Th^{+4} ion and Ox^- ion form soluble structures; the compounds with stoichiometrical formula $[\text{ThOx}]^{+2}$, $[\text{Th}_2\text{Ox}_3]^{+2}$, and $[\text{Th}_3\text{Ox}_5]^{+2}$ were postulated to have the structures



respectively. At a pH of approximately 7 the thorium exists as $-\overset{\text{Th}}{\underset{\text{O}}{|}}-\overset{\text{Th}}{\underset{\text{O}}{|}}-$. The free valences are saturated by oxalate ions, by other hydrated thorium ions, or other anions, for example, nitrate ions. The authors proposed a reaction scheme for neutral solutions as follows. The soluble compounds $\text{Th}_{4n}\text{Ox}_n$, $\text{Th}_{3n}\text{Ox}_n$, and $\text{Th}_{2n}\text{Ox}_n$ can be presented by structures such as shown below (n is an integer which could not be determined by the experimental procedures used; it is used here to indicate that these formulas are merely basic units of a larger structure)



The addition of more oxalate to these soluble oxalate complexes result in the formation of ring structures such as



These authors feel that the course of the reaction depends primarily on the structure of the soluble compounds which are formed quantitatively in the solution before the beginning of the initial precipitation.

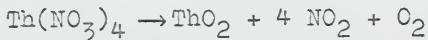
Rombau and Peltier (22) patented a method of preparation of thorium oxide which involved heating thorium oxalate in concentrated ammonium hydroxide, washing, then adjusting the pH of the aqueous suspension of the solid to approximately 2.5, and finally increasing the pH to a predetermined value. They found that the oxide catalyst formed by thermal decomposition at 800°C had the highest surface area when the final pH was adjusted to 6.0. The solid that had a

composition of Th:Ox = 2:1 gave a higher surface area material than a solid of the composition Th:Ox = 1:1 when the final pH was 6.0 for both materials.

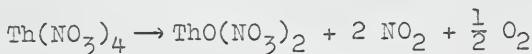
Allred, Buxton, and McBride (23) studied the effect the temperature of the thorium nitrate solution, from which the thorium oxalate was precipitated with oxalic acid, had on the properties of the oxide obtained after thermal decomposition. The material precipitated at increasing temperatures yielded oxides of increasing particle size; however, no change was noted in the particle size or shape with an increase of decomposition temperature from 400 to 900°C. Material from the oxalate precipitated at 10°C gave a cubical shaped particle with an edge-to-thickness ratio of about 3:2; and those from the 100°C material were platelets with edge-to-thickness ratio 6:1. For decomposition temperatures above 600°C, the material precipitated at 40°C produced the solid of highest surface area. The crystallite size as determined by X-ray line broadening was apparently determined by the firing temperature. The authors felt they had obtained a fundamental relationship between the surface area, S, and the crystallite size, D, which was $S = (6/\rho D)(1/F)$ where ρ is the density and $(1/F)$ is a packing factor indicative of the relative crystallite surface area unavailable for nitrogen adsorption in the B.E.T. surface area measurement.

C. Thermal Decomposition of Thorium Nitrate Hydrate

The thermal decomposition of thorium nitrate hydrate has been investigated by Claudel and Trambouze (24). They observed that below 224°C the loss of weight when heated at a rate of 2°/minute was greater under vacuum than at atmospheric pressure; at this temperature the weight-loss curves intersected; and above this temperature the weight loss of the sample heated at atmospheric pressure was larger. They explained this by proposing that at atmospheric pressure the thorium is hydrolyzed by the water of hydration and that the thoria formed from the hydrolysis acts to provide nuclei for de-nitration. They propose that above 224°C the reaction occurring at atmospheric pressure is



while under vacuum these two reactions occur (both slower than the above reaction)



Veron (25) found that the thermal decomposition of thorium nitrate hydrate yielded thoria with a surface area (nitrogen B.E.T.) of $55 \text{ m}^2/\text{g}$ at 600°C , $29 \text{ m}^2/\text{g}$ at 700°C , and $10 \text{ m}^2/\text{g}$ at 900°C .

Winfield (14) found that catalysts prepared by the thermal decomposition of thorium nitrate at 800°C for 50 minutes or by heating successively for 90 minutes at 270°C, 70 minutes at 400°C, and finally 10 minutes at 450°C, were inactive for dehydration of 2,3-butanediol.

D. Chemistry of Aqueous Thorium Salt Solutions

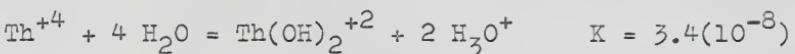
There have been numerous investigations of aqueous thorium salt solutions. These investigations have been undertaken for a variety of motives; one of the most frequent reasons has been for the development of analytical gravimetric procedures where a precipitate of small surface is desirable. There is a general agreement that, while the thorium species Th^{+4} may be present at low pH, more complex species are formed as the OH^- concentration is increased and these species formed are polynuclear thorium complexes. It is the structure and composition of these species that causes controversy. Indeed different workers, studying the same system and obtaining nearly identical experimental results, have proposed quite different polynuclear species as being involved in the equilibria at various pH values. Thus a complete literature survey of thorium ions in solution will not be attempted; but only a few of the more recent publications will be discussed.

Schaal and Faucherre (26) made pH measurements on partially neutralized thorium nitrate and thorium perchlorate

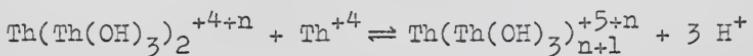
solutions of various concentrations. From these measurements they concluded that the tetramer $\text{Th}_4\text{O}_8^{+8}$ was present over a considerable range of hydrolysis. Souchay (27) obtained evidence for this tetramer in his measurements on the freezing point depressions of thorium nitrate solutions.

Kraus and Holmberg (28) made studies of the change in emf when a known amount of thorium nitrate or perchlorate (with sufficient supporting electrolyte to maintain its concentration at 1 M) was added to solutions at various pH. This change in pH enabled the calculation of the degree of hydrolysis of the thorium species. They concluded that at low pH the principal uncomplexed species of Th(IV) was Th^{+4} (this species is hydrated, that is, $\text{Th}(\text{H}_2\text{O})_x^{+4}$, and they felt that the coordination number should be eight). They back-titrated solutions with initial hydroxyl number $n = \underline{\text{ca.}} 2$ (i.e., $n = \underline{\text{ca.}} 2$ for the reaction $\text{Th}^{+4} + 2n \text{H}_2\text{O} = \text{Th}(\text{OH})_n^{+4-n} + n \text{H}_3\text{O}^+$) and found that equilibrium is rapidly established. This is in marked contrast to two other members of the same "rare-earth" group, Pu(IV) and U(IV); both of these form polymeric materials for $n = \underline{\text{ca.}} 0.5$ and only depolymerize slowly. Hydrolysis of Th(IV) became appreciable near a pH 3. They made no attempt to explain the hydrolyzed species in the region $n > \underline{\text{ca.}} 0.5$ but state only that a large number of species will have to be considered in this region. They assumed the following reactions

to treat the data in the region $n < 0.5$ and calculated equilibrium constants for these reactions.



Hietanen (29) performed potentiometric titrations by adding NaOH to thorium perchlorate in 1 M ClO_4^- solution. He continued the titration until precipitation; at this point the potential began to drift. For thorium concentration of 20 mM a visible precipitate formed at a pH 3.8-3.9; for the concentration 2 mM the solution became opaque at pH 4.7 but the emf became irregular at a pH 3.8. The author concluded that all complexes formed in appreciable amounts can be written in the form $\text{Th}(\text{Th}(\text{OH})_3)_n^{+4+n}$. No n value predominated and no upper limit was found for n but it must be considerably greater than six. A good approximation to the experimental data was obtained if it was assumed that all successive steps in the reaction

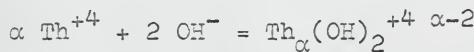


had the same equilibrium constant; $K = 10^{-7.5}$.

Hietanen and Sillen (30) studied the hydrolysis of Th^{+4} in 0.5 or 0.7 M solutions using chiefly the Cl^- of thorium chloride as the ionic medium and limiting themselves to small degrees of hydrolysis. In addition to the species

$\text{Th}(\text{Th(OH})_3)_n^{+4+n}$ found in the preceding publication they found evidence for the complexes $\text{Th}_2(\text{OH})_2^{+6}$ and $\text{Th}_2\text{OH}^{+7}$.

Lefebvre (31) has utilized the pH values from the titrations of Kraus (28) and apparently others and employed a method for calculation which he has called "surface potentiometric titrations." This method derived its name not because of a titration involving solid surfaces but from the fact that he related the pH (or pA) change to the area under a plot of pH versus the concentration of the H^+ ion (or A ion). He found that for a value of n (n = number of hydroxyl groups per thorium atom) less than 0.5 the assumption of Hietanen (29) is not valid and that his proposed species is not present in this area. For the region for $n < 0.5$ one has the equilibrium



and α varies between one and two, that is, the ratio of the species $\text{Th}(\text{OH})_2^{+2}$ and $\text{Th}_2(\text{OH})_2^{+6}$ varies between one and two. In the range $0.5 < n < 2$ Lefebvre found only the species $\text{Th}(\text{OH})_2^{+2}$, $\text{Th}_2(\text{OH})_2^{+6}$, and $\text{Th}_5(\text{OH})_{12}^{+8}$; thus he found only a single complex of the type proposed by Hietanen (29) of the general structure $\text{Th}(\text{Th(OH})_3)_n^{+4+n}$. Lefebvre then considers the region $n > 2$. Here the experimental data are not sufficiently accurate, because of the discontinuity of the potential as one approaches the precipitation point, for exact interpretation. However if the species $\text{Th}_5(\text{OH})_{12}^{+8}$ is

precipitated the equivalence point should be at $n = 2.4$, whereas precipitation occurs near $n = 3$. This shows that the pentacondensed species must disappear as n is increased toward three. The author feels that as one approached $n = 3$ there exists in solution the species $\text{Th}_7(\text{OH})_x$ (where x has any value between 18 and 21) whose concentration becomes noticeable at $n = 2$ and increases rapidly as n approaches three. The following figure presents the results of the author's calculations.

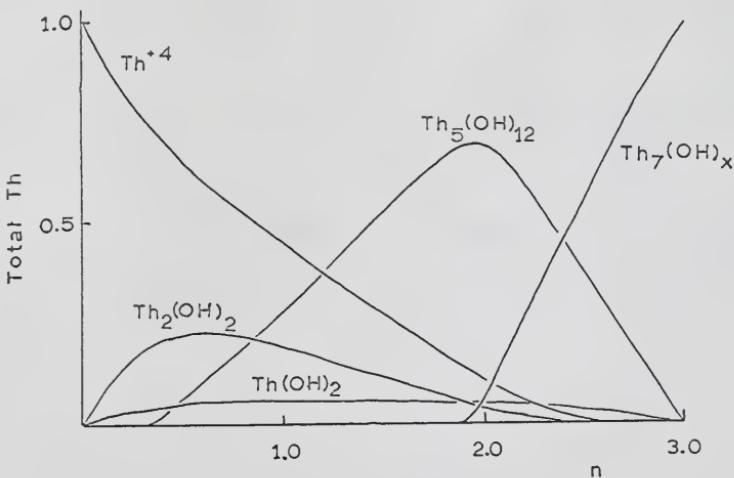


Fig. 1.-Concentration of various thorium species for increasing degree of hydrolysis. (Redrawn from J. Chim. Phys. 55, 227 (1958)).

Lundgren and Sillen (32) determined the structure of $\text{Th}(\text{OH})_2\text{CrO}_4\text{H}_2\text{O}$ by X-ray diffraction. The positions of the Th and Cr atoms were determined by means of the intensities of the X-ray reflection. The positions of the oxygens were obtained by assuming the CrO_4^- group was a regular tetrahedron with Cr at the center, and assuming that the O-O and Th-O bonds have their minimum distances as determined in previous crystal structures. The data led the authors to conclude that the structure of the crystal contained infinite strings of $(\text{Th}(\text{OH})_2)^{+2}_n$ and finite CrO_4^- and water groups. The $(\text{Th}(\text{OH})_2)^{+2}_n$ strings contain almost parallel rows of OH^- groups. The Th atoms are situated on alternate sides of the OH^- "ribbon" in such a way that every Th is in contact with four OH^- (forming almost a square) and every OH^- is in contact with two Th atoms. The Th-O-Th bond length is 2.4 Å. The chain structure is shown below.

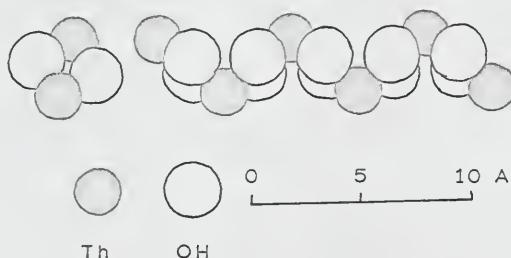


Fig. 2.-The $(\text{Th}(\text{OH})_2)^{+2}_n$ chain viewed along [010] (left) and from the side (right). (Redrawn from Arkiv. Kemi. 1, 277 (1949)).

Lundgren (33) made an X-ray study for $\text{Th}(\text{OH})_2\text{SO}_4$. The only plausible structure that the author could obtain to satisfy the X-ray intensities was very similar to that given above for $\text{Th}(\text{OH})_2\text{CrO}_4\text{H}_2\text{O}$. Again the long zigzag chain of composition $(\text{Th}(\text{OH})_2^{+2})_n$, held together by sulphate ions was proposed.

Larsen and Brown (34) investigated thorium nitrate solutions in dilute nitric and perchloric acids and in pure water by the X-ray radial distribution method using Waser-Schonaker formalism involving pair interaction. They found no indication of the Th-Th bonding indicative of metal ion hydrolysis and polymerization. The radial distribution peaks could be interpreted in the terms of the average features of a distorted antiprism. It was proposed that two nitrate ions are coordinated as bidentate ligands to a central thorium ion with the remaining positions being occupied by water molecules.

Matijevic et al. (35) have investigated the coagulation of silver iodide sols by dilute thorium nitrate solutions at various pH values. At low pH the amount of thorium nitrate required for coagulation agrees with the value calculated by the Schulze-Hardy rule for four-valent counterions. At pH of four the amount of thorium ions required for coagulation increases rapidly until at a pH ~ 7 where it leveled off again at a much higher thorium

concentration. The amount of thorium at pH ~ 7 or higher required for coagulation is just that which is calculated for a trivalent counterion. These authors proposed this trivalent species was $\text{Th}(\text{OH})^{+3}$. At the highest pH range the amount of thorium required dropped sharply suggesting an ion whose valence was even greater than four.

E. Colloidal Thoria

Colloidal thoria sols were prepared over one hundred years ago, for example by Bahr (36), and many methods of preparation have been employed since that time. Two common methods of preparation are considered below. Blitz (37) dialyzed a 14 per cent by weight solution of thorium nitrate and obtained a dilute, water-clear thoria sol containing a small amount of nitrate ion. The sol was determined to be positively charged by electrophoresis, presumably because of adsorption of Th^{+4} or H^+ ions. Electrolysis of the sol caused the particles to be precipitated at the cathode. Müller (38) prepared a more concentrated sol containing approximately 150 g thorium hydroxide per liter. First the thorium was precipitated from the nitrate solution by addition of base. The precipitate was washed thoroughly and then the mixture brought to a boil. A solution of thorium nitrate (200 g thorium nitrate/liter) was added one ml at a time at five minute intervals. After the addition of about 10.5 ml thorium nitrate solution the solution cleared and

had a slightly opaque or turbulent appearance. According to Müller the solid resulting from the evaporation to dryness of this sol is soluble in water whereas the sol prepared according to Blitz's procedure gave an insoluble solid.

A more recent study of colloidal thoria was made by Chun, Wadsworth, and Olson (39). One colloid was prepared by adding thorium nitrate solution to "thorium hydroxide" which had been calcined at 300°C for five hours. Another sol was prepared by treating thorium oxide (from the thermal decomposition of the oxalate) with nitric acid, then repeated drying and slurring in water to obtain a stable sol. Aging studies were then made on 100 ml samples (not stirred while aging) of various concentrations and pH. The particle growth was followed by measuring the decrease of turbidity with time. The sol from "thorium hydroxide" initially had cubic crystallites approximately 30 Å diameter and rather uniform in size; the other sol was cubic and 80 Å in diameter but appeared polydisperse. The electron micrographs indicated the samples were isotropic. The optimum temperature for particle growth was 80°C; essentially no growth occurred at the boiling temperature, at room temperature there was slow particle growth. X-ray studies showed that the crystallite size did not increase, thus particle growth was due to aggregation of crystallites. If particles that were aged in thorium nitrate or potassium nitrate solutions were dried

at 80-90°C and redispersed by adding water the turbidity measurements showed particles essentially the same size as before aging. The initial particle size and rate of growth varied inversely with the thorium concentration; the particle growth also varied inversely with the electrolyte concentration. There was no growth of particles for the 0.2 M sols.

Dobry-Duclaux, Guinand, and Mathieu-Sicard (40) reported filamentous inorganic macromolecules were formed when dilute thorium chloride solutions were hydrolyzed or treated with dilute ammonium hydroxide to incipient precipitation. Electron microscope studies revealed some spheres and filaments from 150 to 2500 Å in length and not over 18 Å thick. Molecular weights of 175,000 and 960,000 were calculated from diffusion experiments but these values are smaller than required for the chain lengths given above. They found that after dialysis the value of n for the compound (-Th(OH)₂O-)_n Th(OH)₃⁺Cl⁻ varied from 6 to 45 for one series and from 7 to 50 for another one.

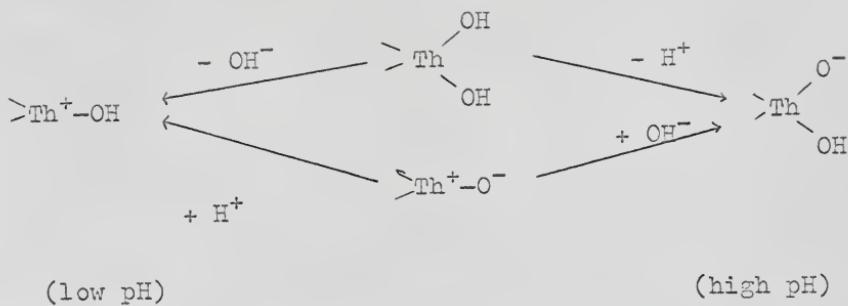
Hentz and Tyree (41) performed light scattering experiments on solutions of thorium-hydroxide-perchlorate with the OH:Th ratio from zero to three. The hydrous oxide was precipitated from a dilute nitrate solution and then washed until the supernatant liquid reached a pH 7-8. This ThO₂ was then dissolved in sufficient perchloric acid to give the desired composition of Th(OH)_n(ClO₄)_x and these

solutions were used as stock solutions; all solutions were clear except the one with $n = 3$ and this one was turbid even after standing three weeks. Aliquots of these stock solutions were diluted to 100 ml to give final concentrations of Th from 0.01 to 0.1 M. All experimental solutions were clear. In none of the series did the degree of polymerization appear to be appreciably concentration dependent. For hydroxyl number, n , 0.0 the degree of polymerization was ca. 0.9 and an unhydrolyzed and uncomplexed species $\text{Th}(\text{H}_2\text{O})_n^{+4}$ was therefore indicated. For $n = 1.0$ a mononuclear species with +1 charge was indicated, and the ion $\text{Th}(\text{OH})(\text{ClO}_4)_2^{+1}$ was suggested. The results at hydroxyl numbers 1.6 and 2.0 indicated the presence of small hydrolytic aggregates with polymerization numbers near 2.3 and 2.9, respectively. These data corresponded closely to the near-neutral species $\text{Th}_2(\text{OH})_4(\text{ClO}_4)_4$ at $n = 1.6$ and $\text{Th}_3(\text{OH})_6(\text{ClO}_4)_6$ at $n = 2.0$; these species have the low charges required for concentration independence for the light scattering experiment. Extremely large aggregates were found at hydroxyl number 3.0. The data indicated a zero charge and polymeric species containing approximately 140-150 thorium atoms per solute particle. They ruled out the possibility of colloidal species at conditions of incipient precipitation because of (a) the constancy of the turbidity of the solutions over repeated ultrafine filtrations; (b) the absence of any dissymmetry of

the scattering particles; and (c) the fact that the refractive index increment was found unchanged when measured before and after all other measurements and operations. The measurements at all concentrations appeared to be equilibrium values although extremely slow processes could not be ruled out.

Zhukov, Onosov, and Kazantsev (42) studied the hydrolysis of thorium ions by adsorption by cation-exchange resins. The sorptive capacity of a KU-1 resin, y , was 2.20 meq/g dry resin. The adsorbability of thorium, x , increased from 1.8 at pH 0.3 to 9.03 meq Th^{+4}/g at pH 3.6. At high pH at the beginning of precipitation the experimental results agree with the compound $(\text{Th}(\text{CH})_4\text{Th})_n^{+4}$, where $n = (x/y) - 1$.

Anderson (43) calculated the ζ -potentials from the measured electrophoretic mobility. Adsorption isotherms were calculated from the ζ -potential by means of the diffuse double layer theory. The thoria was prepared by heating thorium oxalate (precipitated from the nitrate solution at 70°C) at 105°C for 12 hours, 20 hours at 400°C, and 70 hours at 900°C. The electrophoretic mobility was studied at different pH values by using NaOH to adjust the pH. The pH effect was complicated and the author found it necessary to postulate the existence of two pH-dependent dissociation processes schematically visualized as



The Cl^- ion had a higher adsorbability than the NO_3^- ion. The interpretation of the data for the addition of a thorium nitrate solution to the aqueous suspension of thoria was very complicated because there was hydrolysis of the thorium ion. In spite of the hydrolyzed complex the high adsorption of the thorium complex ion was apparent. The maximum value of σ , the electrokinetic surface charge density, in thorium nitrate corresponds to a surface almost saturated (according to a Langmuir surface) with positive charge; upon further increase in concentration marked anion adsorption occurred giving a sharp decrease in the value of σ .

F. X-Ray Investigations of Thoria

Some earlier investigators (44) believed that meta as well as ordinary thorium oxide existed because of the relative ease of solution in acid of some thoria when the sample had been heated to temperatures around 600°C . However Levi and Reiva (45) found from an X-Ray study that the meta oxide had the same crystal lattice dimensions before

and after peptization and that while the meta oxide is more finely sub-divided than the ordinary oxide there was no further sub-division of the individual crystalline granules in the meta oxide.

Winfield (15) found by X-ray examination of thoria prepared from the oxalate at 350°C a "super lattice," also cubic, with a unit cell double the normal thorium oxide dimensions and which corresponded to the thorium oxalate lattice. Winfield concluded that the "porous" lattice of the active thoria was stabilized by the presence of water in "holes" and that removal of this water at higher temperatures led to partial collapse to normal thoria distances (the X-ray lines also became sharper as the sample was heated to 500°C).

Draper and Milligan (46) made X-ray diffraction powder pictures of many thoria samples from the Oak Ridge National Laboratories. They observed that, in addition to the standard lines characteristic of cubical thoria, there were present on nearly all of the negatives additional weak lines at positions corresponding to inter-plane spacings larger than those attributable to thoria. Re-examination of several X-ray diffraction patterns taken previously at the Oak Ridge National Laboratories showed these faint lines on all photographs examined. The lines were present for samples heat treated over a wide range of temperatures, heat treated in

an oxidizing or reducing atmosphere, and samples from various thorium salts. However these lines were not present when the thoria was examined using monochromatix X-radiation from an NaCl crystal nor were these lines present in electron diffraction patterns obtained for the samples. Thus these authors attributed the faint lines to the fact that they were using X-radiation that was not monochromatic.

Chun, Wadsworth, and Olson (39) obtained lines at $2\theta = 16.8^\circ$, 19.7° , and 27.9° as well as the strong thoria peaks at 27.5° , 45.78° , and 54.20° from an X-ray diffraction pattern for colloidal thoria samples aged at pH 0.6 and 1.1 at 90°C . They did not attempt to explain the data in this publication.

G. Studies of Adsorption on Thoria

Chun, Wadsworth, and Olson (47) determined the dehydration kinetics and equilibrium water vapor adsorption by thoria gel prepared from thoria obtained by thermal decomposition of the oxalate similar to the method given in reference 39. Before study the gel was dried at 90°C for 16 hours. Dehydration rates were measured under isothermal conditions by flushing with dry nitrogen. From room temperature to 130°C , a first order dehydration mechanism was found. The enthalpy and entropy was calculated from the rate data on the basis of the absolute reaction rate theory equation. ΔF^\ddagger was calculated from ΔH^\ddagger and ΔS^\ddagger ; its value was not zero

until a temperature of 137°C was reached. These authors concluded that the water is adsorbed by hydrogen bonding to OH^- , NO_3^- , etc., groups and that this water is thermodynamically more stable than liquid water because of its higher entropy in the gel state.

Pearce and Alvarado (48) prepared a thoria catalyst by precipitation from a dilute thorium nitrate solution with ammonium hydroxide, boiling the solution to expel excess ammonia, decanting off the precipitating liquid, and washing eight times. The solid was dried at 120°C for 18 hours, ground and dried at 250°C for 24 hours, re-ground and dried at 250°C for 10 more hours. Adsorption isotherms were measured for ethanol, acetic acid, water, and ethyl acetate at 99.4°C. All adsorption isotherms fit the Freundlich equation (49) except acetic acid. The thoria gel was evacuated at 100°C before running the isotherm.

Hoover and Rideal (50) made a study of the adsorption of nitrogen, hydrogen, ethylene, and ethanol on thoria. The thoria was prepared by precipitation from a hot, dilute thorium nitrate solution with ammonium hydroxide, washing the precipitate free of electrolytes and drying at 120°C. The pressure versus volume adsorbed plots for nitrogen and hydrogen at both 0° and 100°C were nearly straight lines. The adsorption curves for ethanol had discontinuities at both 52.3 and 100°C measurements. Using the Kelvin equation

(49) these discontinuities corresponded to average radii of 5.2 and 14 Å. However, they attributed the first break to completion of the adsorption on an active portion of the surface.

Winfield (15) measured water adsorption isotherms on thoria prepared by the thermal decomposition of washed thorium oxalate at 400°C for six hours. The sample was degassed at 270°C for four to six hours before measuring an isotherm. The author found that the Harkins-Jura equation for a condensed film (49) $\log_{10}(P/P_0) = 0.162 - 1.159/m^2$ (m is the number of millimoles of water adsorbed/gram, P is the pressure, and P_0 is the saturation pressure at the temperature) described the isotherm at high relative pressures. Using this equation a surface area of $95\text{ m}^2/\text{g}$ was calculated. The B.E.T. equation in the range of $P/P_0 = 0.05$ to 0.35 represented the experimental points with a probable error of about 2 per cent. The value $E_1 - E_\infty$, where E_∞ is the heat of liquification of water and E_1 is the average heat of adsorption of the first monolayer, calculated from the B.E.T. equation was 3.3 kcal/mole. The water surface area was $56\text{ m}^2/\text{g}$ using $\sigma = 10.6\text{ \AA}^2/\text{water molecule}$; the nitrogen surface area was only $24.3\text{ m}^2/\text{g}$.

Draper and Milligan (46) measured water adsorption and desorption isotherms for several thoria samples prepared from thorium oxalate calcined at 800°C. They observed that

adsorption was very slow; periods of over fifty hours were required to reach equilibrium. They always found some irreversibly adsorbed water after the adsorption-desorption run. These samples were subjected to four adsorption-desorption runs, the thoria was left under high water pressures for as long as a month for the last two runs. All samples showed an increase of irreversibly adsorbed water after each run; this increase was attributed to some slow aging process. One possible explanation of the slow adsorption equilibrium proposed by the authors was that the thoria had a plate-like structure and diffusion of the adsorbate vapor between the plates was slow. A calculation of pore-size distribution using the Kelvin equation for the desorption curves in the region of hysteresis (P/P_0 ca. 0.35) indicated a large number of pores with 10 Å radius. Water surface areas were calculated to be 10 to 20 m^2/g ; nitrogen surface areas for catalysts prepared similarly are about 10 m^2/g . Adsorption isotherms were run at higher temperatures (175 to 275°C) after evacuation at 700°C; however the amount of adsorption was not very large. Heats of adsorption estimated from these curves are of the order of 20 kcal/mole, suggesting that chemisorption may be occurring. Samples were observed with an electron microscope but the information obtained was limited by the inability to disperse the oxide so that the individual smaller particles could be observed.

Oblad, Weller, and Mills (51) measured the reversible adsorption of water on thoria, obtained by calcining thorium oxalate at 650°C, by passing a nitrogen stream with the desired pressure of water vapor over the thoria sample. The sorption experiments were done at 593°, 538°, and 482°C; then the thoria was heated to 760°C and the sorptions run at 704°, 649°, and 593°C. The surface area (nitrogen B.E.T.) was 30 m²/g initially; after heating to 760°C and concluding the adsorptions the surface area was 12 m²/g. The highest heat of adsorption measured was 40 kcal/mole.

Holmes and Secoy (52) measured the heats of immersion for the thoria-water system. Thoria samples were obtained by calcination of thorium oxalate at 650°, 800°, 1000°, and 1200°C for four hours. The heat of immersion increased with outgassing temperature. Thus they concluded that they were removing progressively more strongly chemisorbed water as well as physically adsorbed gases with increased outgassing temperatures. The heat of immersion increased with increasing specific surface area (water monolayer was estimated from the measured nitrogen surface areas). The dehydration of surface hydroxyl groups appeared to be a reversible process. They observed a "slow heat of immersion," that is, heat was evolved for as long as 90 minutes after immersion; they proposed that this was due to slow diffusion of water into the porous structure of the thorium oxide particle.

Both physical and chemical adsorption have been widely investigated. The theory of adsorption in general has been treated in several review articles (53) and books (54). Therefore even an incomplete survey of the literature on these topics will not be presented in this section.

H. Nuclear Magnetic Resonance Studies of Materials Adsorbed on Solids

The general theory of nuclear magnetic resonance has been presented at various levels of elegance in the past few years (55). Both Neikam (6) and Lawson (5) have reviewed the literature dealing with n.m.r. studies of adsorbate-solid systems. However special mention should be made of a series of publications by workers at the Field Research Laboratory of Socony Mobil Oil Company, Incorporated, who have made both theoretical and experimental spin echo studies of water adsorbed on silica gel catalysts (56). From measurements made at room temperature they have been able to observe relaxation times corresponding to two distinct adsorbed phases. They felt that this two phase system distinguished protons in the water adsorbed in and water adsorbed on the monomolecular layer. Temperature studies from 193° to 374°K were made for these silica samples for various surface coverages. No change of state was indicated near the freezing point of water. The motional phenomena as revealed by relaxation measurements were different for the

two environmental states. The state with the longer relaxation time, state a, exhibited very rapid motion as deduced by both T_1 and T_2 ; the activation energy for this motion was approximately 7 kcal/mole. The low temperature study indicated that the other state (shorter relaxation time, state b) has a very rapid motion as indicated by T_1 and a slow motion as indicated by T_2 . They found that nuclear transfer occurred more slowly than the above motions. At room temperature the effective activation energy for nuclear transfers was about 4.9 kcal/mole; it decreased at higher temperatures and apparently increased somewhat at lower temperatures.

Brey and Lawson (57) made measurements of the average T_1 and average T_2 for water, alcohols, and butylamine adsorbed on various thoria samples as a function of surface coverage and as a function of temperature at particular surface coverages. Their work will be discussed more completely in Chapter V.

CHAPTER III

EXPERIMENTAL

The catalyst preparation methods used for this investigation varied widely. In addition the catalyst preparation methods are a major part of the study; thus the catalyst preparations will be described in a separate chapter.

The nitrogen B.E.T. surface areas were determined by a previously described method (11,58). The catalyst sample was evacuated for two hours at 200°C; the sample weight was not corrected for the loss due to removal of adsorbed materials.

Water B.E.T. surface areas and water adsorption isotherms were measured by directly weighing on an analytical balance the amount of water adsorbed at each pressure. The sample, 2-4 g, was placed in a 50 ml Erlenmeyer flask to which a stopcock had been attached. The sample tube was attached to the adsorption apparatus by a standard taper joint. The sample was evacuated at an elevated temperature, usually 400°C for a four hour period. At each point on the isotherm, after constant pressure readings indicated that equilibrium had been established, the cock was closed, the

bulb removed, grease removed from the joint and the bulb weighed. The pressure was measured by a Zimmerli gauge. No correction was used for the unadsorbed water vapor present in the sample bulb. The adsorption temperature was not controlled precisely; the adsorption temperature was $23^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

The average crystallite size of the catalyst was estimated from the width of the X-ray diffraction line for the (111) crystal plane. The line width was obtained with a Norelco recording diffractometer using copper K_{α} radiation with a nickel filter. The samples were ground to pass through a 400 mesh screen and packed into a shallow sample holder. Crystallite size was calculated using the Scherrer equation (59):

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

where L is the average crystallite dimension perpendicular to the (111) plane which produced the diffraction, k is a constant assumed to be equal to unity (see reference 59 for a discussion of this), and $\beta^2 = B^2 - b^2$, where B is the measured half-width at half-maximum intensity and b is the corresponding value for crystalline ThO_2 (crystalline ThO_2 for these measurements reported for this study was thoria which had been heated at 1200°C).

The magnetic resonance spectra in this study were obtained from a Model 4300-2 Varian Associates spectrometer

container wall. The thermocouple reading was correlated to temperature by comparing the emf of the thermocouple on the sample holder wall to the emf of a thermocouple placed in the sample cavity in an empty sample tube.

A more complete description of the NMR experimental procedure and the determination of T_1 and T_2 is presented in Lawson's dissertation (5).

The NMR catalyst sample, approximately two grams, was placed in a thin walled NMR tube commercially available from Varian. This tube was attached to a vacuum stopcock fitted with a standard taper joint. A small piece of glass wool was placed above the catalyst sample to prevent the catalyst fines from being pumped from the sample tube when the tube was evacuated. Each NMR sample was evacuated and heated to 400°C under vacuum and held at this temperature for four hours. The sample was then removed from the vacuum system, grease cleaned from the joint, and the sample tube weighed on an analytical balance. This weight was used to calculate surface coverages. Water was added in roughly four milligram increments and the nmr signal recorded after each addition until the NMR line width became narrow (about 300 cps); after this a larger amount of water was added each time. At least one day was allowed to elapse between adsorption of the water and recording the NMR spectrum.

operated at a frequency of 56.4 or 60.0 megacycles. The spectra were recorded as the derivative of the absorption signal. The spectrum was recorded at least four times, in most cases the spectrum was recorded six or more times; in all cases the average values of these spectra are recorded in the tables. An exception to this was for catalyst 21-P where the line widths were recorded one or more times at different rates of increasing the static magnetic field. However the line-widths recorded for the line-width versus surface coverages were the average of six or more measurements.

The power level from the transmitter was kept several decibels below that power which gave saturation for the sample. The amplitude of the sweep field used to modulate the static magnetic field as it was being varied through resonance was controlled in order to minimize artificial broadening. The lowest value of the modulation field that would give a measurable signal was used to record the spectrum.

The temperature dependence of the line width was studied using a Varian Model V-4340 variable temperature probe unit. The temperature was controlled by regulating the flow rate of nitrogen gas passing through a copper coil immersed in a liquid nitrogen bath. The temperature of the sample was determined by a thermocouple located on the sample

CHAPTER IV

CATALYST PREPARATION AND NITROGEN B.E.T. SURFACE AREA

The different catalyst activation methods will be described before explaining the catalyst preparation procedures. Most of the catalysts were activated by heating at 600°C under vacuum for four hours. To accomplish this the catalyst material, previously dried at 100°C, was placed in a Vycor tube and the tube connected to a vacuum system by a standard taper joint. The catalyst was evacuated continuously during the activation; the pressure was approximately 0.5-2.0 microns. The activation tube was placed in a furnace and the furnace temperature kept at 600°C by a Wheelco temperature regulator. The furnace temperature reached 400°C in approximately fifteen minutes and 600°C in about 30 minutes; this heat-up time was taken to be a part of the four hour activation period.

The catalysts activated in air were placed in either a Vycor or porcelain boat which was then placed in a 24 mm Vycor tube. This tube was placed in a 10 inch long furnace. The furnace temperature was controlled by a Wheelco temperature regulator. For the first few activations by this method, air, to aid in the oxidation and to carry away decomposition products, was forced through the tube by a

blower; this caused the temperature to fluctuate so greatly that no effort was made to force air over subsequent catalysts during their activation. In addition to this activation method some catalysts were activated in air by placing the material in a porcelain dish in a Hevi Duty Electric muffle furnace. This furnace could not be heated to the activation temperature nearly as rapidly as could the 10 inch furnace.

Some of the catalysts were activated in a water vapor atmosphere. The sample was placed in a porcelain boat in the Vycor tube which was in the 10 inch furnace. In addition to this furnace a six inch pre-heater furnace was placed in front of the main furnace. Steam was generated by boiling water in a flask with a side arm. The main furnace was heated to approximately 100°C and the pre-heater was heated to 250°C before beginning the activation. After the water in the distillation flask was boiling steadily the flask was connected to the Vycor tube and the temperature of the main furnace, which had been heated to 100°C before connecting the steam generator, was increased to 600°C as rapidly as possible. The activation time was four hours and the activation was considered to begin when the temperature of the main furnace was increased above 100°C.

Many of the catalysts had certain steps of their preparation in common. Unless it is stated to the contrary

under the catalyst series preparation the following conditions were used for the catalyst preparations:

(a) The thorium hydroxide* prepared by precipitation was dried at approximately 110°C for 12-24 hours (longer if necessary to obtain a "dry" solid).

(b) Catalysts were activated for four hours at 600°C under vacuum.

(c) Wash procedure employed for precipitated catalyst series from series 4 through 13 was: 200 ml distilled water was added to the precipitate, the mixture was stirred for about five minutes with a mechanical stirrer to obtain a slurry, the precipitate was allowed to settle, and then the liquid was siphoned off. This procedure was repeated until the desired amount of washing was accomplished. At pH below about 7.0 the precipitate began to settle so slowly that some of the very small particles were lost when the liquid was siphoned off.

Therefore a modification of the above procedure was used for the precipitated catalyst series 14 and all subsequent precipitated series. Instead of allowing the gel to settle after stirring the wash water was removed by vacuum

* The precipitate obtained by adding base to a thorium solution will be referred to as thorium hydroxide even though this material is not a hydroxide in the ordinary sense; many authors consider the precipitated material to be hydrous thorium oxide.

filtration using Whatman #42 filter paper. This filter paper retained all visible thoria precipitate except for some of the catalysts prepared by precipitation at the lowest pH values at which precipitation occurred.

(d) The solid $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ is very hygroscopic and it is unlikely that the material used in these studies had this formula; the water content was probably greater than given by this formula. However this formula weight was used for the calculations unless it is stated that the thorium content was determined gravimetrically. The thorium nitrate used was the Fisher Certified Reagent grade obtained from the Fisher Scientific Company.

(e) The ammonium hydroxide was Baker and Adamson, reagent grade, containing 28-30 per cent NH_3 and was used as received unless stated otherwise for the particular catalyst preparation.

A. Catalyst 3

Eighty grams of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in 1000 ml distilled water. One hundred ml concentrated ammonium hydroxide was added rapidly to the stirred (by hand rather than by the mechanical stirrer) solution. The gel was divided into equal portions and the washing was done by putting 100 ml water on the precipitate filter cake and allowing to filter by gravity. The nitrate test was by the standard brown ring test (60). The following results were obtained:

Catalyst	Wash, ml	Final pH	NO_3^- Test	Surface Area*
3-A	50	9	Positive	0.52, 0.41
3-B	100	8	Positive	9.4
3-C	150	8	Positive	7.95, 7.13
3-D	200	7	Positive	10.7
3-E	500	6-7	Negative	6.75, 6.05
3-F	1000	5-6	Negative	14.3
3-H	None	--	--	7.1
3-I	None	--	--	2.1

B. Catalyst 4

Sixty g of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in 750 ml of distilled water. One hundred ml aliquots of this solution were removed and precipitation was effected by dumping 10 ml of the concentrated ammonium hydroxide into the stirred (by hand) solution. Each catalyst was washed with 1000 ml of distilled water by adding 200 ml portions on top of the filter cake of thorium hydroxide and allowing to filter by gravity. The surface areas for these catalysts were:

Catalyst	Surface Area
4-A	10.9
4-B	16.7
4-C	17.6
4-D	22.3
4-E	21.7
4-F	16.8
4-G	21.7

Eighty g of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in 1000 ml distilled water and the hydroxide was precipitated by dumping 100 ml concentrated ammonium hydroxide into the solution which was stirred with a mechanical stirrer. The surface areas were:

* All surface areas in this chapter have units of m^2/g .

Catalyst	Surface Area
4-K	29.6
4-L	31.6
4-M	27.9

C. Catalyst 5

Catalysts 5-A, -B, and -C were prepared from a solution of 8 g of thorium nitrate tetrahydrate per 100 ml water; the remaining catalysts were precipitated from a solution of 70 g thorium nitrate tetrahydrate per liter of solution. The method of precipitation and washing was as follows (100 ml thorium solution was used for each catalyst):

- 5-A Precipitated by adding 10 ml concentrated ammonium hydroxide in approximately three minutes and washed with 800 ml of water.
- 5-B Precipitated by slowly adding 10 ml concentrated ammonium hydroxide to the stirred solution in about one hour and washed with 600 ml water.
- 5-C Slowly precipitated by adding just enough concentrated ammonium hydroxide to the stirred solution in 15 minutes to cause the thick gel formation (see discussion section) and washed with 200 ml water.
- 5-D Same as 5-C except washed with 400 ml water.
- 5-E A portion of the catalyst 5-D precipitate was washed with 200 ml of dilute ammonium hydroxide (5 ml concentrated ammonium hydroxide in 195 ml of water) and then washed with 1800 ml water.
- 5-F Precipitated by dumping 10 ml concentrated ammonium hydroxide into the thorium solution and then the slurry was stirred for one hour; the precipitate was washed with 1000 ml water.
- 5-G Precipitated by adding dropwise in four minutes 10 ml concentrated ammonium hydroxide and washed with 100 ml water.

5-I, 5-H Enough concentrated ammonium hydroxide was added to cause thick gel formation; washed with 400 ml water.

5-J Ten ml concentrated ammonium hydroxide was added in 50 minutes and washed with 1000 ml water.

5-K Ten ml concentrated ammonium hydroxide was added in 25 minutes and washed with 1000 ml water.

Catalyst	Surface Area	Catalyst	Surface Area
5-A	2.6	5-G	7.5
5-B	0.6	5-H	1.0
5-C	15.0	5-I	4.0
5-D	28.6	5-J	0.5
5-E	0.8	5-K	0.9
5-F	24.2		

D. Catalyst 7

These catalysts were prepared from thorium oxalate which was precipitated from an acid solution with oxalic acid (61). The precipitation was carried out at approximately 50°C in a solution approximately 1 N in nitric acid by the addition of a 5-10 per cent excess of an oxalic acid solution over a 10 minute period. The catalysts prepared from washed thorium oxalate were prepared from the same thorium oxalate as the other catalysts below except that the thorium oxalate was washed ten times with distilled water.

7-A Thorium oxalate was thermally decomposed by heating under vacuum by slowly increasing the temperature in 100°C increments each hour to 600°C and held at this temperature for six hours. The catalyst was very black after this treatment.

7-B About 3.5 g of catalyst 7-A was placed in about 200 ml distilled water and heated at 70°C for two and one-half hours. The catalyst was then dried at 110°C.

- 7-C Thorium oxalate was placed in a porcelain dish and put in a 18 mm Vycor tube. The temperature was increased by increments as follows: kept at 100°C for one hour, then increased by 100°C increments each 30 minutes until 600°C was reached. The temperature was kept at 600°C for six hours.
- 7-E Thorium oxalate was placed in the boat in the Vycor tube and the temperature increased to 600°C as rapidly as the furnace could attain this temperature and then heated at 600°C for six hours.
- 7-F Prepared the same as 7-E; after solid cooled to room temperature it was heated in 200 ml water for three hours at 70-80°C. The surface area was determined after drying at 100°C; then sample was heated to 600°C for two hours.
- 7-G Thorium formate was prepared from thorium nitrate and formic acid by preparing a concentrated solution of these compounds and the water was allowed to slowly evaporate. The thorium formate crystals were then recovered from the saturated solution and dried at 50°C. This thorium formate was thermally decomposed the same as was 7-E.
- 7-H The furnace was heated to 600°C and then the boat containing the thorium oxalate was placed in the furnace as rapidly as possible. The temperature dropped to 500°C but rapidly increased to 600°C. The sample was heated at this temperature for six hours.
- 7-I Thorium oxalate which had been washed with de-ionized water was thermally decomposed by the same method as was used for catalyst 7-H.
- 7-J Thorium oxalate was heated from room temperature to 600°C; then heated at this temperature for six hours.
- 7-K Washed thorium oxalate was heated from room temperature to 600°C, then was heated at this temperature for six hours.
- 7-L Washed thorium oxalate was heated at 970°C for four hours.
- 7-M Three g of thorium oxalate and 0.075 g of ammonium nitrate were mixed together by grinding; the mixture was placed in a boat and heated at 600°C for four hours.

- 7-N Thorium oxalate was heated to 600°C in air and heated at this temperature for four hours. The surface area was determined; then the catalyst was heated in distilled water at 80°C for four hours and re-heated at 600°C for two and one-half hours.
- 7-O Three g of washed thorium oxalate and 0.3 g of ammonium nitrate were mixed by grinding; the mixture was heated at 600°C in air for four hours.
- 7-P Washed thorium oxalate was heated in air at 600°C for four hours.
- 7-R A mixture of 2.6 g washed thorium oxalate and 0.63 g ammonium nitrate was heated at 600°C for four hours in air.
- 7-S A mixture of 4.1 g washed thorium oxalate and 0.01 g ammonium nitrate was heated at 600°C for four hours in air.
- 7-T A mixture of 3 g washed thorium oxalate and 0.074 g ammonium nitrate was heated at 600°C for four hours in air.
- 7-U Pills were prepared from unwashed thorium oxalate by compressing under 90,000 p.s.i. and these pills were heated to 600°C in a stream of oxygen, then they were heated for four hours at 600°C under vacuum.
- 7-V Same as 7-U except pills were heated under nitrogen to 600°C rather than oxygen.
- 7-W Same as 7-U except pills were heated to 600°C under vacuum.

Catalyst	Surface Area	Catalyst	Surface Area
7-A	17.7	7-M	38.9
7-B	21.6	7-N	37.8**
7-C	18.1	7-O	27.8
7-E	29.9	7-P	18.0
7-F	37.4*	7-R	34.3
7-G	30.6	7-S	14.0
7-H	35.2	7-T	25.6
7-I	15.8	7-U	16.8
7-J	33.0	7-V	1.8
7-K	12.2	7-W	1.5
7-L	2.3		

*Surface area after heating at 600°C a second time; after drying at 110°C the surface area was 35.4.

**Surface area after heating to 600°C a second time; after drying at 110°C the surface area was 38.4.

E. Catalyst 8

Forty g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in 500 ml of distilled water and precipitated by dumping 50 ml concentrated ammonium hydroxide into the stirred (mechanical) solution. The precipitate was filtered and divided into six equal portions and washed as follows:

Catalyst	NO_3^- Test	Ml Wash	Ml Wash/g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$	pH	Surface Area
8-A	Positive	200	30	9	1.05
8-B	Positive	400	60	9	13.0
8-C	Positive	600	90	9	13.3
8-D	Positive	1000	150	7-8	22.1
8-E	Uncertain	1200	180	5	20.4
8-F	Uncertain	1400	210	5	22.8

F. Catalyst 9

Sixty-five g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in enough water to give 375 ml of solution. Aliquots of this solution were then diluted as described below and each aliquot was precipitated by dumping into the stirred solution 10 ml of concentrated ammonium hydroxide.

Catalyst	Dilution	Resulting Molarity	Ml Wash	Surface Area
9-A	None	0.30	1800	34.8
9-B	37.5 to 75	0.15	1800	28.6
9-C	37.5 to 137	0.08	1800	18.6
9-D	37.5 to 188	0.06	1800	9.3
9-E	37.5 to 375	0.03	1800	1.1
9-F	37.5 to 750	0.015	2000	1.0
9-G	37.5 to 1500	0.0075	2200	1.1

The following catalysts were prepared by the same procedure as given above except a stock solution of 60 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$

was dissolved in enough water to make 60 ml of solution.

Catalyst	Dilution	Resulting Molarity	ml Wash	Surface Area
9-K	None	1.8	1200	15.9
9-L	10 to 15	1.35	1200	22.0
9-M	10 to 20	0.90	1200	27.4
9-N	10 to 30	0.60	1200	31.2
9-O	10 to 40	0.45	1200	33.5
9-H	No dilution, heated to 70°C before precipitation, washed with 400 ml acetone.			2.9
9-I	Dilution was 37.5 ml to 75 ml, precipitated at 70°C, mixture heated at 70°C for one hour, and washed with 1200 ml water.			32.5
9-J	Same as 9-I except the hour heating period was eliminated from the procedure.			25.2

G. Catalyst 10

Forty g of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was dissolved to make 500 ml stock solution which was used to prepare the following catalysts.

- 10-A One-half ml of concentrated ammonium hydroxide was slowly added to 100 ml of the stock solution; then precipitation was completed by dumping 10 ml concentrated ammonium hydroxide into the mixture; washed with 1400 ml water.
- 10-B Same as 10-A except one ml of concentrated ammonium hydroxide was added slowly before the rapid precipitation.
- 10-C Same as 10-A except two ml of concentrated ammonium hydroxide was added slowly before the rapid precipitation.
- 10-D Same as 10-A except three ml of concentrated ammonium hydroxide was added slowly before the rapid precipitation.

Catalyst	Surface Area
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10-A	27.7
10-B	30.5
10-C	23.4
10-D	9.9

H. Catalyst 11

One hundred ml aliquots of a stock solution of 40 g of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ per 500 ml were precipitated by dumping the amount of concentrated ammonium hydroxide indicated below into the stirred thorium solution.

Catalyst	Ml Ammonium Hydroxide	Ml Wash	Surface Area
11-A	7	1200	24.4
11-B	5	1200	8.3
11-C	15	1600	39.4
11-D	20	1600	38.2
11-E	30	2800	41.2
11-F	50	3000	37.6
11-G	100	3000	41.7

I. Catalyst 12

One hundred sixty-six g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was dissolved in enough water to make one liter of solution. The thoria was precipitated by dumping 200 ml concentrated ammonium hydroxide into the solution. It was necessary to divide the gel into two equal portions before washing due to the bulk of the precipitate. Each portion was washed twelve times with 600 ml portions of water. The catalysts were prepared by activation as described below.

Catalyst		Surface Area
12-A	600°C under vacuum for four hours	37.8
12-B	400°C " " " "	65.9
12-C	500°C " " " "	53.5
12-D	700°C " " " "	18.9
12-E	800°C " " " "	0.9
12-F	600°C in air for four hours	31.0
12-G	400°C " " " "	57.0
12-H	500°C " " " "	49.5
12-I	700°C " " " "	3.5
12-J	600°C under water vapor for four hours	28.6
12-K	400°C " " " "	60.8
12-L	500°C " " " "	42.7
12-M	700°C " " " "	11.8
12-N	900°C " " " "	0.5
12-O	800°C " " " "	1.1
12-P	500°C " " " "	40.5
12-Q	600°C under vacuum for four hours	27.8

J. Catalyst 13

The thorium hydroxide was prepared by dumping 200 ml of concentrated ammonium hydroxide into 1000 ml of a solution containing 166 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$. The precipitate was divided into six equal portions and washed with the amount of water shown below.

Catalyst	Ml Wash Water	Ml Wash/g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$	Surface Area
13-A	200	24	13.7
13-B	400	48	31.4
13-C	500	60	31.8
13-D	600	72	38.8
13-E	800	96	33.8
13-F	1600	192	31.3

K. Catalyst 14

Eighty grams of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in enough water to make 350 ml of solution. This was precipitated by

dumping 200 ml of concentrated ammonium hydroxide into the stirred solution. The precipitate was collected by filtration, then 300 ml of water was added to the solid. This mixture was stirred for 10 minutes and two aliquots, containing as nearly as possible 1/9th and 1/8th of the total thorium, respectively, was removed from the slurry while stirring. The remaining thoria precipitate was collected by filtration and then placed in 400 ml water and the mixture again slurried by stirring for 10 minutes. This time an aliquot was removed which contained 1/7th of the remaining thorium since two samples were removed from the first washing. This washing and removing aliquots was continued until all of the precipitate was washed.

Catalyst	Total Water Added	Ml Wash/g Th(NO ₃) ₄ ·4 H ₂ O	Surface Area
14-A	300	3.8	1.0
14-B	300	3.8	1.0
14-C	700	10.2	28.9
14-D	1100	18.1	36.2
14-E	1500	27.6	44.4
14-F	1900	39.7	42.1
14-G	2300	56.4	38.4
14-H*	2700		32.0
14-I*	3100		33.4

*Heated 15 hours instead of 4 hours.

L. Catalyst 16

These catalysts were prepared by precipitating different concentrations of thorium nitrate solutions with 1.14 times the theoretical amount of ammonium hydroxide by dumping

the required amount of ammonium hydroxide into the stirred thorium solution. The thorium nitrate concentration was determined by precipitating the thorium as the oxalate and igniting the thorium oxalate at 1000°C for 24 hours.

Catalyst	Thorium Concentration, M	ml Wash Water	Surface Area
16-A	0.282	600	<0.5
16-B	0.217	800	<0.5
16-D	0.0575	800	<0.5
16-H	0.0199	800	<0.5
16-J	0.0121	800	<0.5

M. Catalyst 17

- 17-A Eighty ml of a 0.282 M thorium nitrate solution (thorium concentration determined by precipitation as the oxalate for this series of catalysts) was diluted to 800 ml and the thorium precipitated by adding 250 ml 0.286 M ammonium hydroxide over a 5 minute period. After 220 ml was added the solution was merely cloudy; there was complete precipitation after the addition of 250 ml of ammonium hydroxide. Precipitate was washed with 200 ml of water.
- 17-B Forty ml of 0.282 M thorium nitrate solution was diluted to 400 ml and precipitated by adding in 5 ml increments a total of 125 ml of 0.286 M ammonium hydroxide. The precipitate was washed with 200 ml water.
- 17-D One hundred thirty ml 0.286 M ammonium hydroxide was added to a solution of 40 ml 0.282 M thorium nitrate diluted to 400 ml. Washed with 200 ml water.
- 17-F One hundred forty ml 0.286 M ammonium hydroxide was added to a solution of 40 ml 0.282 M thorium nitrate diluted to 400 ml. Washed with 600 ml water.
- 17-G Same as 17-F except 40 ml 0.282 M thorium nitrate was diluted to 800 ml.
- 17-I Same as 17-F except 40 ml 0.282 M thorium nitrate was diluted to 150 ml.

- 17-J Forty ml 0.282 M thorium nitrate was diluted to 1600 ml and 140 ml 0.286 M ammonium hydroxide was added. This amount of base did not cause precipitation or even cause the solution to become cloudy; 20 ml of 0.286 M base was then added and precipitation was complete. Washed with 600 ml water.
- 17-K Seventeen and one-half ml 0.646 M thorium nitrate solution was diluted to 400 ml and 127 ml 0.319 M ammonium hydroxide was slowly added. Washed with 400 ml water.
- 17-L Thirty-five ml 0.646 M thorium nitrate solution was diluted to 800 ml and 255 ml 0.319 M ammonium hydroxide was slowly added. Precipitate was collected and was added to 200 ml wash water. This mixture could not be filtered and was dried at 110°C without removal of the wash water.

Catalyst	Surface Area	Catalyst	Surface Area
17-A	57.2	17-I	<0.3
17-B	39.6	17-J	<0.3
17-D	<0.3	17-K	<0.3
17-F	<0.3	17-L	39.9
17-G	<0.3		

N. Catalyst 18

One hundred twenty g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was dissolved in enough water to make 525 ml solution. The thorium was precipitated by dumping 300 ml concentrated ammonium hydroxide into the stirred solution. The precipitate was collected by filtration, slurried with 400 ml water, and filtered. A portion of the precipitate corresponding to as nearly 1/9th of the total was removed for catalyst 18-A. The rest of the precipitate was slurried with 400 ml of water and the above procedure repeated until all the precipitate had been used.

Catalyst	Ml Wash Water/g Th(NO ₃) ₄ •4 H ₂ O	Surface Area
18-A	3.33	1.0
18-B	7.08	6.1
18-C	11.4	33.0
18-D	16.3	47.3
18-E	22.3	46.7
18-F	29.7	44.8
18-G	39.4	41.6
18-H	53.7	42.1
18-I	84.0	39.2

O. Catalyst 20

- 20-A Fifty ml 0.646 M thorium nitrate was added dropwise to 480 ml of 0.310 M ammonium hydroxide. Mixture was heated at 100°C for 10 minutes.
- 20-B Fifty ml of 0.646 M thorium nitrate was added dropwise to 480 ml of 0.310 M ammonium hydroxide. Mixture was heated at 80°C for 30 minutes.
- 20-C Same as 20-B except mixture was not heated after precipitation.

All three catalysts described above were washed with 800 ml of a solution containing 12 ml of concentrated ammonium hydroxide.

Catalyst	Surface Area
20-A	23.4
20-B	11.7
20-C	12.1

P. Catalyst 21

- 21-A Twenty ml 0.646 M thorium nitrate solution (determined gravimetrically) was diluted to 400 ml and 140 ml 0.319 M ammonium hydroxide was added. The pH was 6.0-6.1 and precipitation of thorium was not complete. The precipitate was collected but when the precipitate was heated to 110°C to dry the solid re-dissolved. No precipitation occurred even after nearly all of the water was evaporated and the solution was cooled to room temperature. The solid was collected by evaporation to dryness.

- 21-B Twenty ml 0.646 M thorium nitrate solution was diluted to 400 ml and enough 0.319 M ammonium hydroxide was added to give a final pH of 7.0. The precipitate was washed with 200 ml water.
- 21-C Same as 21-B except final pH was 8.5.
- 21-D Same as 21-B except final pH was 8.4 and 600 ml wash water was used.
- 21-E Same as 21-B except final pH was 7.95 and 800 ml wash water was used.
- 21-F Twenty-five ml 0.646 M thorium nitrate solution was diluted to 400 ml and enough 0.319 M ammonium hydroxide was added to give a final pH of 9.0. Washed with 800 ml water.
- 21-G Same as 21-F except final pH was 10 and 1000 ml wash water was used.
- 21-H A solution of 40 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ in one liter of water was precipitated by adding enough ammonium hydroxide to give a final pH of 7.0. The very thick gel formed at a pH 5.8. The precipitate was washed twice; first with 800 ml water and then with 500 ml. The precipitate dissolved when heated at 100°C. The pH of the solution after dissolving the solid was 3.1. The pH of the solution was re-adjusted to 7.3 with ammonium hydroxide and the precipitate collected and dried at 110°C.
- 21-J Ammonium hydroxide was added to 25 ml of 0.646 M thorium nitrate solution to give a pH of 9.3; then nitric acid was added to give a final pH of 6.9. Precipitate was washed with 200 ml of wash water.
- 21-K Ammonium hydroxide was added to 25 ml of 0.646 M thorium nitrate solution to give a pH of 9.3; then nitric acid was added to give a final pH of 7.9. Precipitate was washed with 200 ml wash water.
- 21-L Approximately 4 g of catalyst 21-H solid, dried overnight at 110°C, was added to 300 ml water and the mixture was heated at the boiling point for three hours. The pH was 2.5 at a solution temperature of ca. 50°C. The undissolved solid was collected and washed with about 500 ml of water while on the filter pad.

- 21-M Approximately 4 g of catalyst 21-H solid, dried overnight at 110°C, was added to 300 ml water and the mixture was heated at the boiling point for three hours. The pH was 2.9 at a temperature ca. 50°C. Enough ammonium hydroxide was added to give a pH of 7.5 at a solution temperature of ca. 50°C.
- 21-N About 4 g of catalyst 21-H solid, dried at 110°C overnight was added to 300 ml water and the mixture heated at the boiling point for three hours. Then 700 ml water was added and the mixture heated overnight. pH before mixture was heated overnight was 3.5. After heating overnight ca. 4 g of thorium nitrate tetrahydrate was added during a 15 minute period and the mixture heated for 48 hours; water was added to keep the volume at one liter. The pH at the end of the heating was 3.5. The undissolved solid was collected by filtration and this solid was used for catalyst 21-N.
- 21-O Enough ammonium hydroxide was added to the filtrate from the preparation of catalyst 21-L (which was milky in appearance) to increase the pH from the original 3.5 to a final pH of 7.4.
- 21-P Enough ammonium hydroxide was added to the filtrate from the preparation of catalyst 21-N to increase the pH from the original value of 2.1 to 7.2. The solid was dried at 85°C overnight and the solid redissolved. Enough ammonium hydroxide was added to this solution to give a pH of 7.2 and the mixture was heated for about four hours near the boiling point; then the precipitate collected by filtration. Solid was dried at 100°C without dissolving.

Catalyst	Surface Area	Catalyst	Surface Area
21-A	26.8	21-H	90.0
21-B	59.6	21-J	<0.5
21-C	<0.5	21-K	<0.5
21-D	<0.5	21-L	69.5
21-E	<0.5	21-M	78.6
21-F	5.88	21-N	69.6
21-G	4.35	21-O	110
		21-P	114

Q. Catalyst 22

Thirty g of unwashed thorium oxalate (same as used for catalyst series 7) was slurried in 400 ml water and 50 ml concentrated ammonium hydroxide was added to this slurry. The mixture was heated at approximately 90°C for about two hours. The solid was collected and added to a nitric acid solution whose concentration was such that the final pH was between 2.5 and 3.0 and a volume about 1500 ml. This mixture was heated for approximately one and one-half hours. The mixture was cooled to about 60°C and divided into four equal portions. Each portion was used to prepare one of the four catalysts given below.

- 22-A Enough ammonium hydroxide was added to the mixture to give a final pH of 9.0. The solid was washed with 800 ml water.
- 22-B Enough ammonium hydroxide was added to the mixture to obtain a final pH of 6.0; the precipitate was washed with 600 ml water.
- 22-C Enough ammonium hydroxide was added to the mixture to give a final pH of 7.0; solid was washed with 600 ml water.
- 22-D Enough ammonium hydroxide was added to the mixture to give a final pH of 8.0; solid was washed with 800 ml water.

The four catalysts described above were activated for four hours at 600°C in air; the sample was heated in a Vycor boat in the 10 inch furnace as described at the beginning of this chapter.

Twenty g of thorium oxalate was heated in about 200 ml concentrated ammonium hydroxide for about one hour. The solid was collected and heated for about two hours in a nitric acid solution at a pH of 2.5. This mixture was then cooled to about 50°C and enough ammonium hydroxide added to give a final pH of 7.0. The solid was washed four times with 400 ml of wash water each time. This solid was used to prepare the catalysts listed below.

- 22-F Approximately 3 g of the solid was heated at 800°C in air for eight hours in the small furnace in a quartz tube.
- 22-G About 3 g of the solid was heated at 800°C in a muffle furnace for seven and one-half hours.
- 22-H About 3 g of the solid was heated at 700°C for four hours in the quartz tube.

Catalyst	Surface Area
22-A	46.6
22-B	49.3
22-C	51.3
22-D	48.4
22-F	20.0
22-G	10.7
22-H	16.6

R. Catalyst 23

A rapidly precipitated thorium hydroxide solid was prepared by dumping 200 ml concentrated ammonium hydroxide into a solution of 80 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ in 500 ml water. The slowly precipitated solid was prepared by adding 200 ml concentrated ammonium hydroxide over an hour period to the same thorium concentration as was used for the rapidly

precipitated thorium solid. The thick gel formed when about 25 ml of the base had been added. These solids were used to prepare the following catalysts.

- 23-B Solid from rapid precipitation was heated at 600°C under vacuum for four hours; solid was not washed before activation.
- 23-C Approximately 7 g of the rapidly precipitated hydroxide solid was added to 200 ml water and the mixture was heated at approximately 90°C for two hours. The pH at the end of the heating was 3.8; sufficient ammonium hydroxide was added to the slurry to obtain a pH of 7.0. The precipitate was washed with 200 ml of water.
- 23-D Same as 23-C except the slowly precipitated solid was used. The pH at the end of the heating period was 3.2.
- 23-E Same as 23-C except was filtered after heating without adding any base and the solid collected was used as sample 23-E.
- 23-F Same as 23-D except was filtered after heating without adding any base and the solid collected was used as sample 23-F.

Catalyst	Surface Area
23-B	<1.0
23-C	90.6
23-D	86.5
23-E	80.0
23-F	83.6

Attempts were made to prepare a slurry of both the slowly and the rapidly precipitated hydroxide with a pH of 2.5 by adding nitric acid without heating the mixture. In both cases all of the solid dissolved before a pH of 2.5 was reached.

S. Catalyst 24

- 24-A Approximately 65 ml of a 30 per cent hydrogen peroxide solution was added to a solution of 25 ml 0.646 M thorium nitrate in 200 ml of water. The solid was collected by filtration and dried in air for three days, then at 100°C for about 12 hours.
- 24-B Approximately 8 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was added to 25 ml of water and then 500 ml of isopropyl alcohol added to the solution. Concentrated ammonium hydroxide was added slowly until the solution became cloudy. Then approximately 20 ml concentrated ammonium hydroxide was rapidly added. The precipitate was washed three times with 300 ml portions of water each time.

A stock solution was prepared by dissolving 40 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ in 100 ml of water and this stock solution was used for catalysts 24-C through 24-G. All catalysts were precipitated by dumping 10 ml of concentrated ammonium hydroxide into the stirred mixture of the stock solution and alcohol.

Catalyst	Ml Stock Sol'n	Ml Isopropyl Alc.	Ml Wash Water	Surface Area
24-C	20	100	600	50.5
24-D	20	250	600	67.0
24-E	20	500	600	62.7
24-F	20	1000	1000	7.6
24-G	20	2000	1000	0.8

A stock solution was prepared by dissolving approximately 20 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ in the minimum amount of water possible (approximately 20 ml total solution) and this was used to prepare the catalysts listed below.

- 24-H Fifteen ml concentrated ammonium hydroxide was dumped into a mixture of 4 ml stock solution and 21 ml dioxane. Washed with 400 ml water.

- 24-I Fifteen ml concentrated ammonium hydroxide was dumped into a mixture of 4 ml stock solution, 6 ml water, and 15 ml dioxane. Precipitate was washed with 400 ml water.
- 24-J Fifteen ml concentrated ammonium hydroxide was dumped into a mixture of 4 ml stock solution, 11 ml water, and 10 ml dioxane. Washed with 400 ml water.
- 24-K Fifteen ml concentrated ammonium hydroxide was dumped into a mixture of 4 ml stock solution, 16 ml water, and 5 ml dioxane. Washed with 400 ml water.
- 24-L Approximately 4 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was dissolved in 35 ml dioxane and 15 ml concentrated ammonium hydroxide was dumped into the solution. Washed with 400 ml water.

Catalyst	Surface Area
24-A	5.2
24-B	75.8
24-H	16.9
24-I	40.5
24-J	37.8
24-K	39.3
24-L	14.6

T. Catalyst 25

- 25-A About 3 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated to 600°C rapidly in the 18 mm Vycor tube in the 10 inch furnace and kept at this temperature for twenty-four hours.
- 25-B About 5 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated in the muffle furnace to 600°C. The furnace temperature was about 100°C when the sample was placed in it; the temperature was increased to 400°C in about four hours with the door open; then heated to 600°C with door closed. Heated at 600°C for twenty-two hours.
- 25-C Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was placed in the muffle furnace with the furnace temperature 400°C and the door left open until the oxides of nitrogen ceased to be evolved, then heated to 600°C; heated at this temperature for sixteen hours.

- 25-D Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was placed in a Vycor boat in a 24 mm Vycor tube about 12 inches in length and heated as rapidly to 600°C as the furnace could do so (ca. 15 minutes) and heated at this temperature for twenty-four hours.
- 25-E Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was placed in muffle furnace at 600°C and was heated at this temperature for twenty-four hours.
- 25-F Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was placed in muffle furnace at 615°C and sample was heated at this temperature for five hours.
- 25-G Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated in a Vycor boat in the 24 mm tube to 200°C , left at this temperature for approximately 25 minutes; then heated to 250°C (oxides of nitrogen were given off during this heating period) and left at this temperature for about 15 minutes; then heated at 300°C for approximately 10 minutes; then the temperature was increased to 600°C and the sample heated at this temperature for eighteen hours.
- 25-H Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated in the muffle furnace, beginning at room temperature and attaining 600°C in about five hours, for a total of fourteen hours.
- 25-I Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated to ca. 225°C in air in a Vycor boat in a 24 mm diameter Vycor tube; heated at this temperature for ca. 20 minutes; then heated at 300°C for ca. 45 minutes, and then heated at 600°C for four hours.
- 25-J Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated at 75°C for two hours, then at 150°C for one hour, then at 180°C for one and one-half hours, then at 240°C for 15 minutes (decomposition to give oxides of nitrogen during this period), and then at 600°C for seven hours.
- 25-K Sample of $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ was heated under vacuum to 195°C , the temperature dropped back to 180°C quickly and was kept at this temperature for 15 minutes; then was heated to 600°C in air and held at this temperature for four hours.

25-L Prepared by decomposing $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ by dropping the solid into a porcelain dish at red heat. This catalyst was very bulky for its weight and appeared very crystalline (see reference 62).

Catalyst	Surface Area	Catalyst	Surface Area
25-A	28.2	25-G	55.5
25-B	14.6	25-H	20.7
25-C	17.1	25-I	38.4
25-D	29.0	25-J	35.4
25-E	<1.0	25-K	<1.0
25-F	<0.5	25-L	9.3

U. Catalyst 26

26-A Distilled ammonium hydroxide* was used to precipitate a solution of 8 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ in ca. 200 ml of water. Precipitation was by dumping the base into the stirred solution. Precipitate was washed six times with 200 ml portions of water. The solid would not dissolve in water even after heating at the boiling point for 24 hours. Small portions of thorium nitrate tetrahydrate were added until about 6 g had been added; after these additions the solution was water clear rather than cloudy. Distilled ammonium hydroxide was added to give a final pH of 6.9. This solid dissolved when it was heated to 100°C to dry. About one-half of this solution was used to prepare catalyst 26-A; the pH of this portion of the solution was increased to 7.0. This solid dissolved when dried; the solution was heated to "dryness."

*Baker and Adamson reagent grade concentrated ammonium hydroxide was vacuum distilled at room temperature; the distillate was diluted with about five times its volume of distilled water.

26-B Distilled ammonium hydroxide was added to 30 ml of a thorium chloride** solution. The solid was washed four times with ca. 200 ml water each time. This solid would not dissolve in water after it had been heated at 100°C overnight even after boiling for 24 hours. Then 25 ml of the thorium chloride solution, in about 5 ml increments, was added to the boiling mixture. The solid still would not dissolve. The

26-B (cont'd)

solid material was collected by filtration and was used for catalyst 26-B.

**Eighty g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ was precipitated by addition of ammonium hydroxide and washed by the siphoning method used in the earlier catalyst preparations until the precipitate began to peptize. The solid was then dissolved in concentrated hydrochloric acid, evaporated to dryness; the solution in concentrated acid and evaporation process was repeated two more times. The solid was then dissolved in enough water to give 500 ml of solution.

26-C The pH of the liquid from catalyst 26-B preparation was adjusted to 7.5; the solid was washed with 400 ml of water.

26-J Approximately 10 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{H}_2\text{O}$ in 300 ml of water was precipitated by adding distilled ammonium hydroxide to give a pH of 7.0. The solid was washed with 200 ml of water.

26-K Distilled ammonium hydroxide was added to 1/4^{lb} of the colloidal sol obtained in the preparation of catalyst 26-A to give a final pH of 8.5. Solid was not washed.

26-L Distilled ammonium hydroxide was added to 1/4^{lb} of the colloidal sol obtained in the preparation of catalyst 26-A to give a final pH of 6.5. Solid was not washed; it dissolved when dried at 110°C.

Fifty ml of the thorium chloride solution** was diluted to give a volume of 200 ml and then concentrated ammonium hydroxide added to give the final pH as shown below.

Catalyst	pH	Ml Wash Water	Surface Area
26-D	5.5	No wash	7.5
26-E	6.5	200	9.1
26-F	7.1	200	19.6
26-G	7.6	400	29.1
26-H	8.5	800	22.0
26-I	10.0	800	2.0

Catalyst	Surface Area
26-A	<0.5
26-B	28.6
26-C	38.4
26-J	72.5
26-K	89.4
26-L	76.4

V. Catalyst 30

Thorium hydroxide was precipitated from a solution of 80 g $\text{Th}(\text{NO}_3)_4 \cdot 4 \text{ H}_2\text{O}$ in 500 ml water using a great excess of concentrated ammonium hydroxide. The sample contained so much ammonium nitrate that it could not be dried at 100°C. The sample was put in water and reprecipitated with ammonium hydroxide. The solid was washed once with 400 ml of water. It was dried at 110°C. The sample was put in one liter of water and heated for 48 hours. Most of the material had not dissolved after this heating. Then 30 ml 0.646 M thorium nitrate solution was added in 5 ml increments over a two day period; the mixture was kept at the boiling point during these additions. Some of the solid still had not dissolved after this treatment; the mixture was separated and used to prepare the following catalysts.

- 30-B The pH of about 1/4th of the solution, after removal of the insoluble solid, was adjusted from an initial value of 1.8 to a final value of 7.0 by the addition of ammonium hydroxide. The solid was not washed.
- 30-C Same as 30-B except the final pH was 8.5 and solid was washed with 200 ml of water.

- 30-D Same as 30-B except material was precipitated by dumping 100 ml concentrated ammonium hydroxide into the solution; solid was washed with 800 ml of water.
- 30-E Same as 30-B except final pH was 9.5 and solid was washed with 200 ml of water.
- 30-G A portion of the insoluble solid was put in ca. 150 ml of water and the pH of the suspension adjusted to 6.9.
- 30-H A portion of the insoluble solid was put in ca. 150 ml of water and 30 ml concentrated ammonium hydroxide was added rapidly.

Catalyst	Surface Area
30-B	5.0
30-C	62.2
30-D	74.0
30-E	79.5
30-G	<1.0
30-H	<1.0

CHAPTER V

PRESENTATION AND DISCUSSION OF RESULTS

A. General

As indicated in the Introduction much of the study of heterogeneous catalysis has been, and still is to a great extent, a poorly defined scientific discipline. One reason for this is the enormous complexity of a heterogeneous solid; indeed the defects present in a so-called perfect crystal have not been elucidated completely at this time. In 1954 Emmett wrote, in the preface of volume I of his series of books "Catalysis" (53c): "In the past, catalysis has been correctly designated as an art. Those who have sought to improve catalysts have, accordingly, had to depend largely on empirical correlations and on a large measure of intuition in using effectively the mass of experimental results that have appeared in the literature. However, within the last thirty years, the art has gradually been acquiring a considerable coating of scientific luster Though catalysis has not been placed on a firm scientific foundation, the signs of progress are numerous and unmistakable."

One reason for little discussion of the catalyst preparation method in early catalytic studies, such as with

thoria was the belief that the metal oxide, for example, thoria, had the same properties regardless of the source. Even after Taylor (63) proposed the heterogeneous nature of catalysts and Adkins (64) proposed that reactions such as dehydration were effected by the "porous" structure of the catalytic material, investigators had no way of measuring these properties. However, as early as 1925 investigators began to attempt a measurement of the surface by adsorption measurements. The first attempts utilized chemisorption and in a few special cases these were successful, but in general there was uncertainty as to whether the monolayer was completed or whether more than a monolayer was adsorbed. Then in 1938 Brunauer, Emmett, and Teller (4) derived the B.E.T. equation for multilayer adsorption. This derivation required assumptions whose justification has been criticized by many authors (53). However, the equation has been applicable between relative pressures of about 0.05 to 0.35 for nearly all solids studied to date and has yielded very reproducible results when employed by different workers in various laboratories. The B.E.T. method agrees well with those derived from other viewpoints, for example, Harkins-Jura method (49). The present situation for the B.E.T. equation seems to be that while the derivation is not rigorously correct, the equation provides the best or at least as good a method for the calculation of the true surface area of a solid as is available at the present time.

In general one would not expect the activity of a catalyst to be proportional to the surface area. Many catalytic reactions are believed to be limited to certain active spots on the surface. Also, for a very porous material, not all of the surface may be equally accessible to the reactant. A good correlation is shown by the catalytic activity of chromia-alumina catalysts for the dehydrogenation of butane (53c); in this case the activity of a catalyst may be accurately obtained by merely measuring the surface area. In instances where the reaction takes place only on certain points, especially where the catalyst is not a single oxide, the agreement is not as good as in the above case. However, it has usually been found that the larger surface area catalysts are more active than the ones with low surface areas. While Legg (3) did not make reaction runs over catalysts with a wide range of surface areas, he did find that the higher surface area thoria, prepared by precipitation, was more active for the dehydrogenation-dehydration of alcohols.

The nitrogen adsorption isotherm for catalyst 12-B is presented in Figure 3. This isotherm has a shape which might be interpreted to be a Langmuir isotherm, that is, a Type I isotherm by Emmett's classification. If this is the case a plot of P/V versus P should be a straight line with a slope equal to the monolayer volume, V_m ; as seen in Figure 4 this is not the case. Figure 5 is the B.E.T. plot for

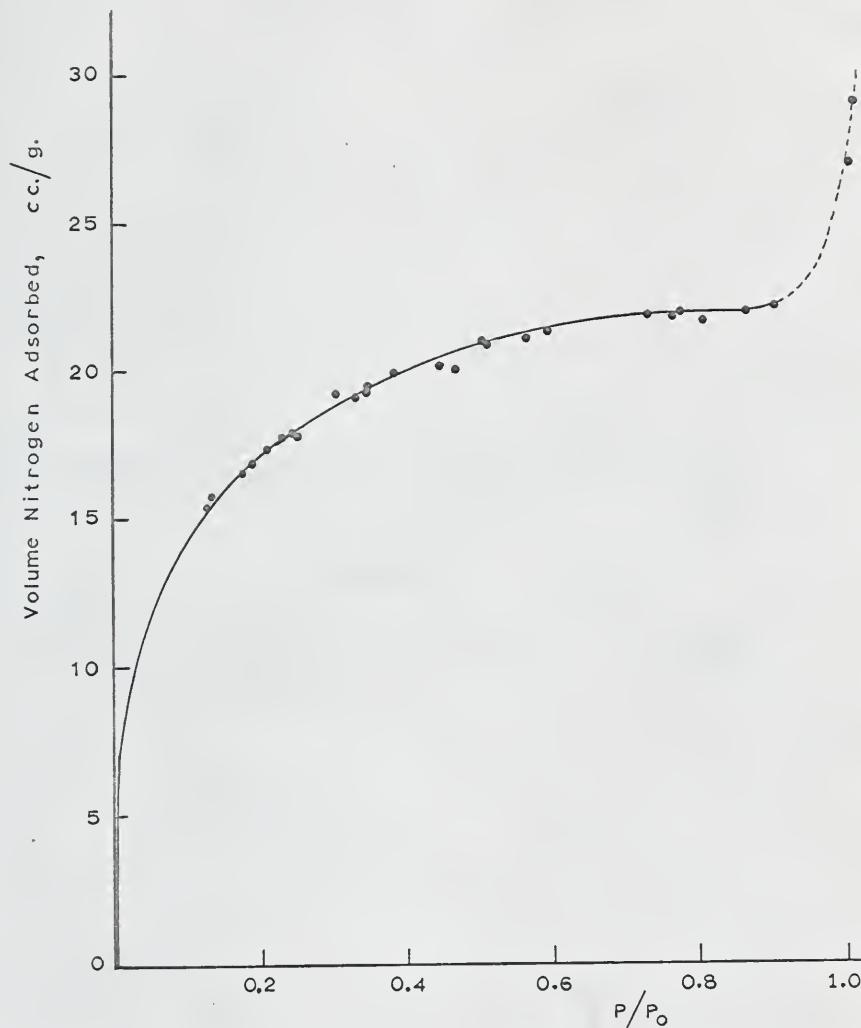


Fig. 3.-Nitrogen adsorption isotherm at the boiling point of nitrogen for catalyst 12-B.

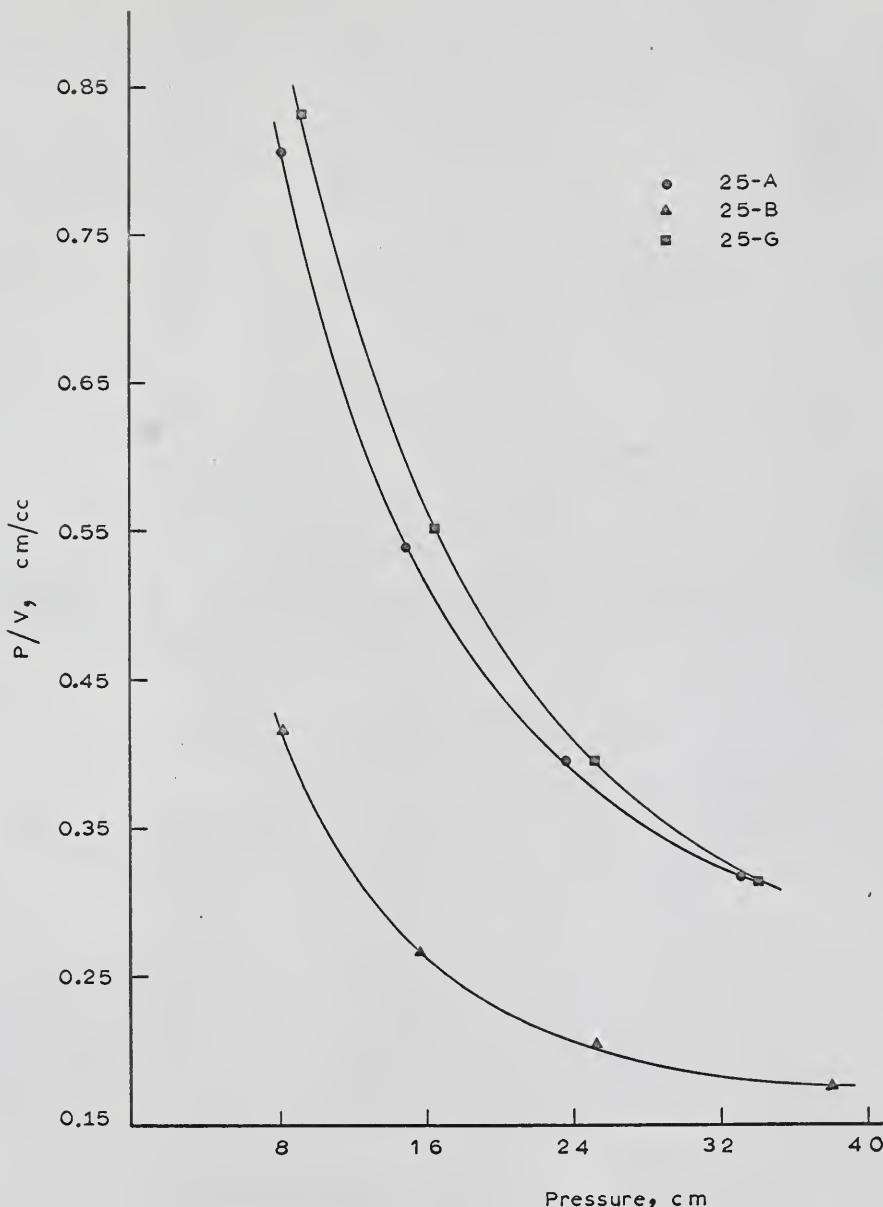


Fig. 4.-Plot of P/V vs. P for the Langmuir isotherm for catalyst series 25.

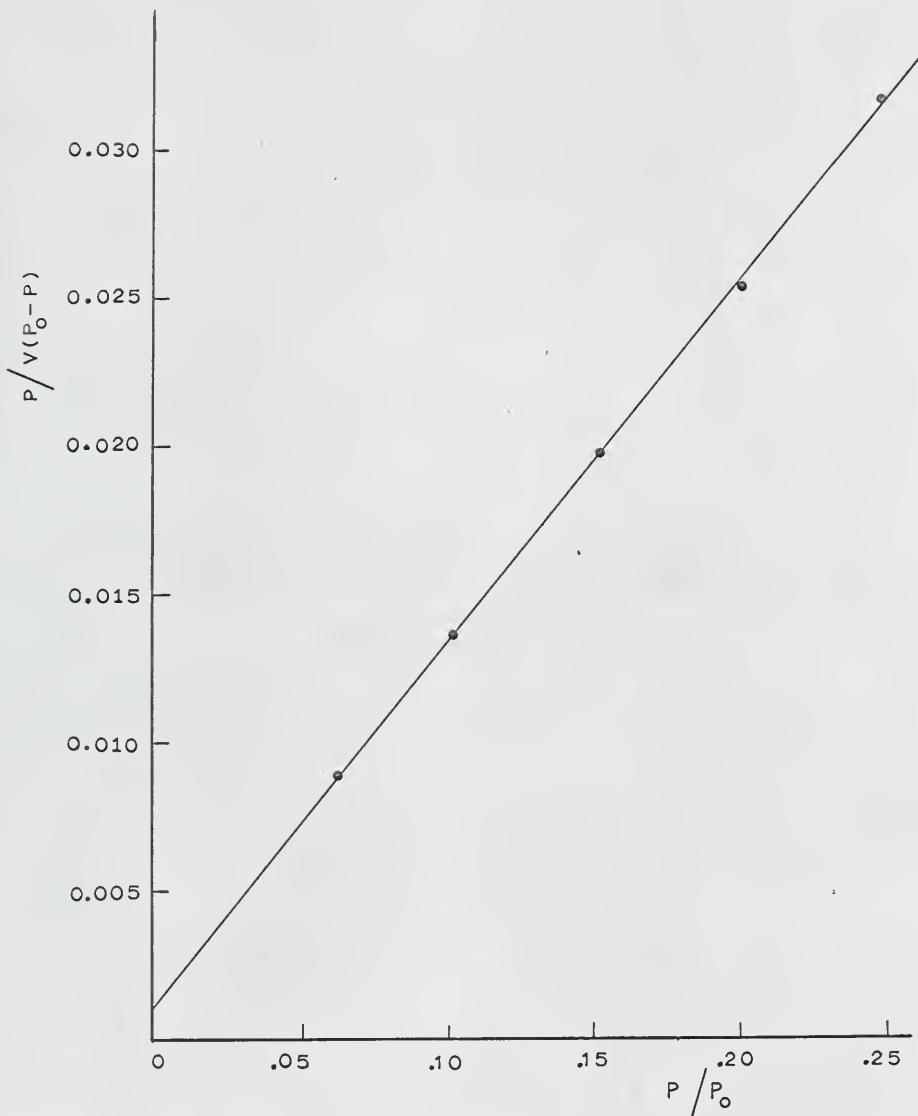


Fig. 5.-Plot of the linear form of the B.E.T. equation for catalyst 13-E.

nitrogen adsorption at its boiling point for catalyst 13-E. The experimental points determine a straight line as predicted by the B.E.T. theory for multilayer adsorption.

B. Oxalate Catalysts

All catalysts for series 7 were prepared by the thermal decomposition of thorium oxalate. Thermal decomposition under vacuum does not appear to be a satisfactory preparation method. The catalyst prepared from the pelleted material had a very low surface area; the one prepared from the powder had relatively high area but the catalyst appeared to be contaminated with carbon. A determination of the CO_2 evolved when the catalyst was heated to 950°C for a few minutes in oxygen showed 1.0-1.5 per cent carbon was present; however, some of this could have been present as the carbonate rather than carbon. These results indicate that, at least for the un-washed thorium oxalate, the surface areas produced are higher the more rapidly the sample is heated to 600°C . Also, the washed thorium oxalate produces thoria whose maximum surface area is only one-half the maximum surface area obtained from un-washed thorium oxalate. Thorium formate (containing some nitrate) yielded thoria whose surface area was comparable to the thoria from un-washed thorium oxalate. It is also noted that the thoria

from un-washed thorium oxalate heated slowly to 600°C, from un-washed thorium oxalate heated under vacuum to 600°C, and from the washed thorium oxalate all had approximately the same surface areas.

It is seen that the addition of ammonium nitrate to washed thorium oxalate increased the surface area obtained. Indeed, the addition of 0.63 g ammonium nitrate to 2.6 g of washed thorium oxalate produced a surface area as large as that obtained by a similar decomposition of the un-washed thorium oxalate. The thorium oxalate to which ammonium nitrate was added should have essentially the same amount of water present as the washed thorium oxalate; hence it is not likely that the increased surface area is due to the water of hydration. Thus it is believed that it is the ammonium nitrate itself, or more specifically the oxides of nitrogen, which causes the surface area increase.

It is known that oxides of nitrogen are able to catalyze oxidations; for example, the oxidation of gaseous SO_2 , by the formation of intermediate compounds with the oxygen. Thus it might be possible for the decomposition to follow a different reaction path in the presence of oxides of nitrogen.

At the slow rate of heating and heating under vacuum the ammonium nitrate could vaporize and distill from the heated portion of the tube before the decomposition temperature of the thorium oxalate is reached. After heating the

oxalate to which ammonium nitrate had been added, one could see solid ammonium nitrate condensed on the cooler part of the reaction tube after the activation was completed. Thus the slow decomposition, decomposition under vacuum, and decomposition of the washed oxalate all take place in an atmosphere with little or no oxides of nitrogen present and consequently the complete oxidation would be slower than with the nitrogen oxides present. This still does not explain why the rapid decomposition leads to a higher surface area; one possible explanation would be that the slower decomposition enables the thoria to form more nearly its normal crystal structure. If this were the case one would expect the low area catalysts to have larger crystallite sizes; catalysts 7-K and 7-O fit this pattern but not enough crystallite sizes have been measured in this series to decide if this is the case.

Whatever the mechanism might be for producing high surface thoria it is evident that the nitrogen compounds present act to enhance the surface area. This is also evident from a plot such as that made by McBride et al. (23) of the surface area versus the average X-ray crystallite size. The low surface area materials prepared by activation of washed thorium oxalate, by slow thermal decomposition, and activation under vacuum gave material which did give a straight line plot, as shown in Figure 6. Indeed, even a

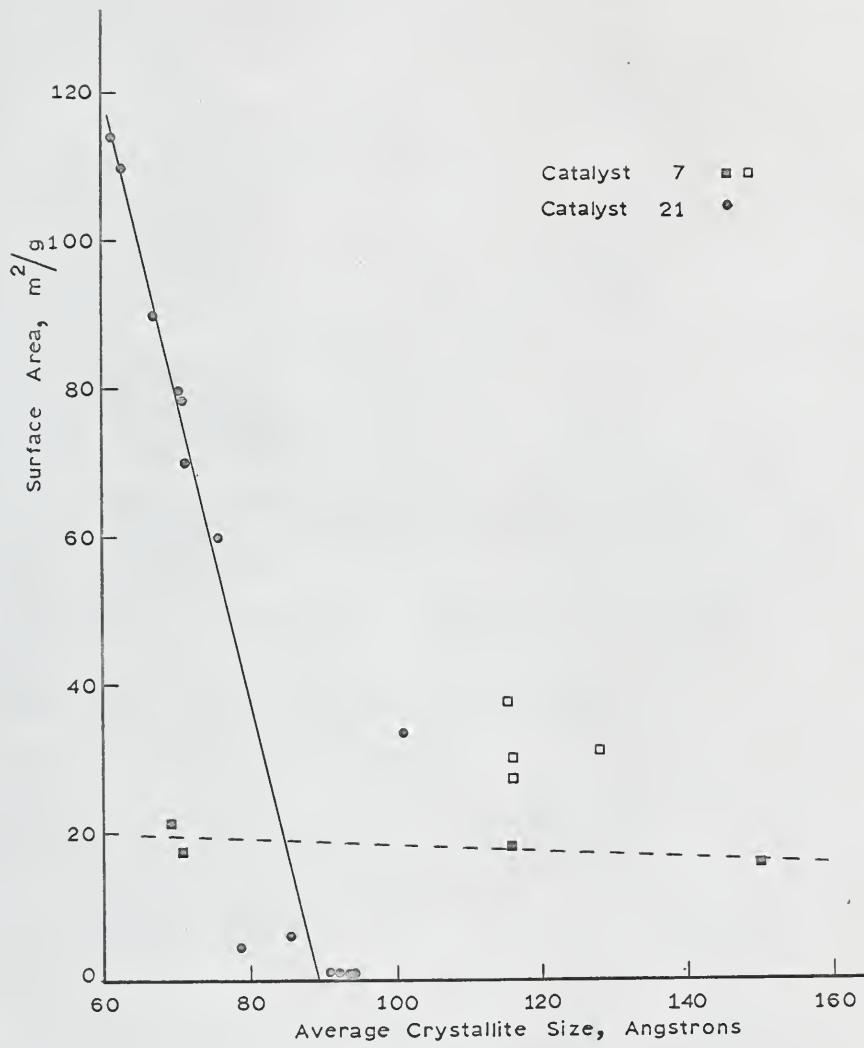


Fig. 6.-Plot of surface area vs. average crystallite size for catalyst series 7 and 21.

catalyst activated by heating slowly at 700°C fitted this curve. The material from the un-washed oxalate came much closer to falling on the theoretical curve calculated according to the McBride *et al.* equation than on the curve defined by those samples for which the nitrogen oxides probably had little effect.

Some of these catalysts which were heated in water and then outgassed at 200°C before determining the B.E.T. surface area had the same area as before heating in water; re-heating to 600°C under vacuum likewise did not alter the initial surface area.

C. Preparation of Thoria by Thermal Decomposition of Thorium Nitrate Hydrate

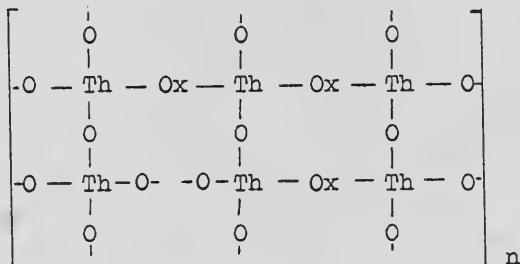
The preparation of thoria catalysts by the thermal decomposition of the hydrated thorium nitrate is in agreement with Veron (25). The decomposition under vacuum leads to a low surface area material while the proper decomposition in air leads to a high surface area material. This is most easily explained as has been done by Claudel and Trambouze (24); that is, some of the water of hydration dissolves the thorium nitrate. This is further supported by the results of the present work. It was found that the rate of heating is very important; indeed, surface areas of less than $1 \text{ m}^2/\text{g}$ were obtained by the very rapid decomposition. Also a slow rate of heating produced a low area material as indicated by

catalyst 25-B. Apparently this slow rate of heating allowed too much of the water of hydration to be lost before the decomposition began; that the loss of water is sufficient to produce a low area material is demonstrated by catalyst 25-K which was heated to 200°C under vacuum before decomposition in air. In addition to the requirement found previously (25), that the decomposition must take place in air to produce a high area material, it is found that the rate of heating is critical. Not enough is known about even the stoichiometry of the material present when decomposition occurs to speculate as to the path of the thermal decomposition of the hydrous thorium nitrate.

D. Preparation of Thoria from Thorium-Oxalate-Hydroxide

Thoria samples were prepared by the method patented by Rombau and Peltier (22). No evidence was noted for a maximum surface area at a pH of 6; samples precipitated at pH from 6 to 9 had nearly the same surface area. These catalysts had higher areas than thoria obtained by the decomposition of essentially pure hydrated thorium oxalate. According to Rombau and Peltier the solid prepared as was done in the present study contains only approximately one-fourth of the theoretical amount of oxalate required to form $\text{Th}(\text{C}_2\text{O}_4)_2$. Thus the solid has a formula ca. $\text{Th}_2(\text{OH})_6(\text{C}_2\text{O}_4)$. If it is assumed that the precipitation by oxalate is

reversible, that is, oxalate ions can be replaced by OH^- ions and vice versa the solid which is in contact with the supernatant liquid, then the structure of a solid of this composition would be



In a basic solution such as was used in the preparation of these catalysts one should expect the bridging groups to be oxo instead of ol groups.

This structure does not have thorium present in the eight coordination state unless water of hydration is present. However if this plate-like two-dimensional structure remained after thermal decomposition, it would yield a structure which could explain water adsorption isotherms which were obtained for these samples.

The past history of the precipitated solid hydroxide used for the patented procedure was not stressed by these authors. However, this study shows that the hydroxide solid behaves quite differently than the oxalate solid and the past history of the hydroxide is very important in determining the surface area of the solid obtained.

E. Preparation of Thoria from the Precipitated Hydroxide

Moreland (11) observed that the rate of addition of base for the precipitation of thorium hydroxide* from the nitrate solution as well as the amount of washing affected the surface area of the thoria obtained after activation by heating at elevated temperatures. Catalyst series 3 shows that the amount of washing apparently affects the surface area; however, no conclusions could be made since the surface area did not change uniformly with washing. Moreland likewise was not able to obtain a consistent relationship for the surface area with increased precipitate washing.

Catalyst series 4 shows that the method of washing for series 3, that is, adding 200 ml portions of water to the precipitate filter cake, and allowing to filter by gravity, does not give reproducible results. For catalyst series 4 a large portion of thoria was precipitated and the precipitate-supernatant liquid mixture divided into nearly equal portions and each catalyst washed the same way. After activation the surface areas were found to range from 10.9 to $22.3 \text{ m}^2/\text{g}$. The activation method, heating at 600°C under vacuum for four hours, was found to be quite reproducible; the surface areas for a thoria sample precipitated, washed, and dried at 100°C as one batch but then divided into three

* See footnote, page 41.

portions and activated separately gave surface areas of 14.9, 15.2, and $14.1 \text{ m}^2/\text{g}$. Since the catalysts for series 4 were precipitated together the only variable in their preparation should have been the washing each one received. The same procedure was used for three other catalysts except the washing procedure used was to add 200 ml of wash water, stir with a mechanical stirrer, allow the precipitate to settle, and then the liquid siphoned off; this wash procedure was repeated five times. The surface area for these three catalysts was 29.6, 31.6, and $27.9 \text{ m}^2/\text{g}$. It was later found that an even more reproducible washing method was adding water, stirring with a mechanical stirrer and filtering, reslurrying and repeating the procedure.

Catalyst series 5 shows the effect of the rate of addition of an excess of ammonium hydroxide to the thorium nitrate solution. All of the catalysts prepared by the slow addition of a considerable excess of concentrated ammonium hydroxide have a low surface area. The catalyst prepared by dumping 10 ml concentrated ammonium hydroxide into the stirred thorium nitrate had an area of $24.2 \text{ m}^2/\text{g}$, the area of the one where the addition of 10 ml of base was over a four minute period was $7.5 \text{ m}^2/\text{g}$; for the addition over longer periods, the area was less than $1 \text{ m}^2/\text{g}$.

The effect of washing can be seen in Figure 7. It is seen that the surface area of the thoria increases rapidly

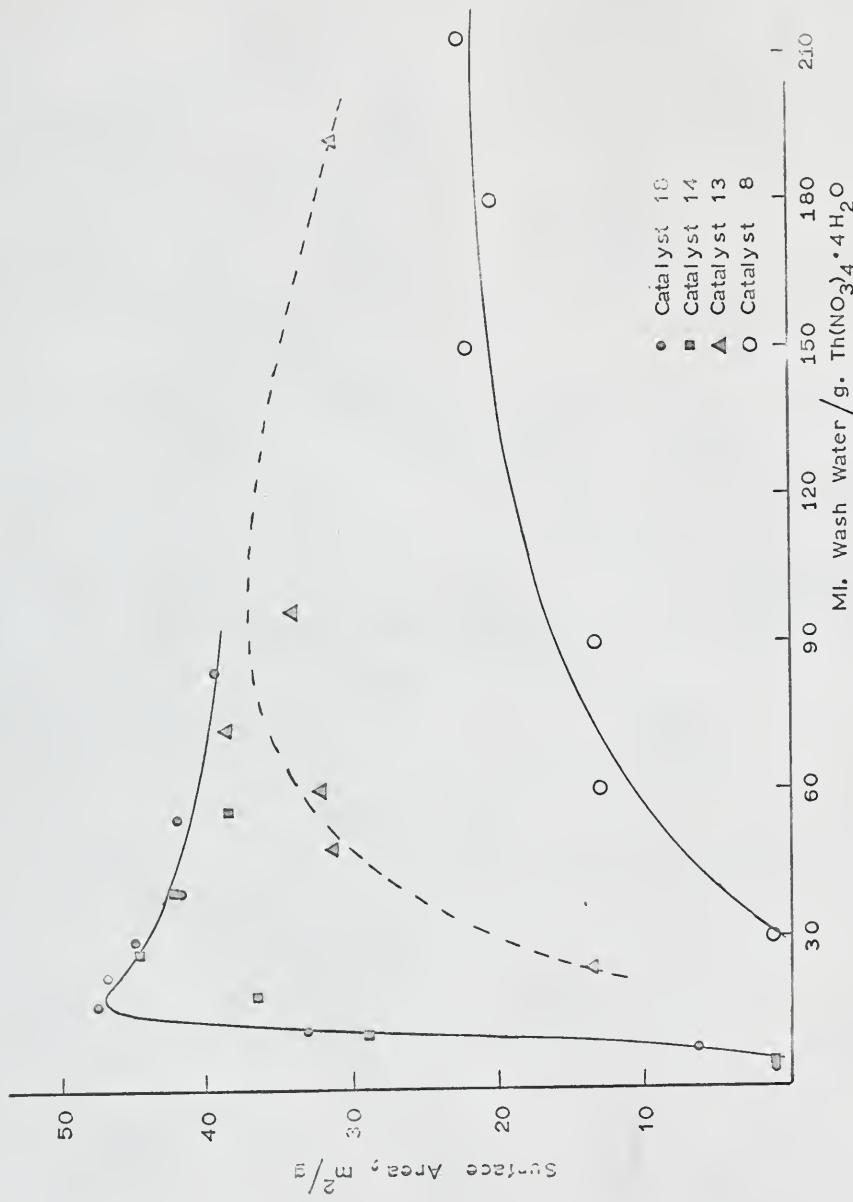


Fig. 7.—Effect of washing catalyst precipitate on surface area.

during the early stages of precipitate washing. Catalyst series 8 was washed by dividing the precipitated solid into six equal portions and washing each portion with different amounts of water by repeatedly slurring the solid with 200 ml of wash water, stirring, and siphoning off the wash water. Series 13 was prepared and washed by the same procedure as series 8 except the thorium concentration for the former was 0.27 M while for the latter it was only 0.15. Catalyst 14 was precipitated from a 0.41 M thorium solution. The entire precipitate was slurried with 300 ml water and stirred with a mechanical stirrer for 10 minutes. During the stirring a portion of the suspension was removed and the precipitate of this portion collected by filtration, dried, and activated. The water was siphoned from the remaining solid and again slurried with 400 ml water and the washing cycle repeated. Peptization became noticeable after washing with a total of 1500 ml of water; the precipitate removed at this time had the maximum surface area. Catalyst 18 was prepared by precipitation from a solution with the same thorium concentration as for catalyst 14. However, instead of siphoning off the wash water after each stirring, the wash water was removed by filtration; a portion of this gel was dried and activated; the remaining gel was again slurried and the washing processes repeated. The agreement of the results for series 14 and 18 is surprising in view

of the experimental difficulties encountered in making reproducible washings, that is, siphoning off equal amounts of water each time, filtering to the same "dryness" each time, and also removing the same amount of catalyst precipitate each time since the ml of wash/g was calculated assuming an equal amount of material was removed each time.

It is also noted that the material for which the maximum surface is higher requires a smaller amount of washing to attain this maximum value of surface area. 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.

These results agree with Moreland's conclusions if additional stipulations are added. The slow addition of base produces a low surface area catalyst provided an excess of base is added. If a sufficient excess is added a great amount of washing will not yield a catalyst with a surface area as large as $2-3 \text{ m}^2/\text{g}$. His other conclusion that washing increases the surface area is supported for the early stages of washing; prolonged washing will cause a decrease in surface area, particularly for hydroxides which produce a high maximum surface area thoria.

In Figure 8 the effect of the thorium nitrate concentration on the surface area is shown. All catalysts were

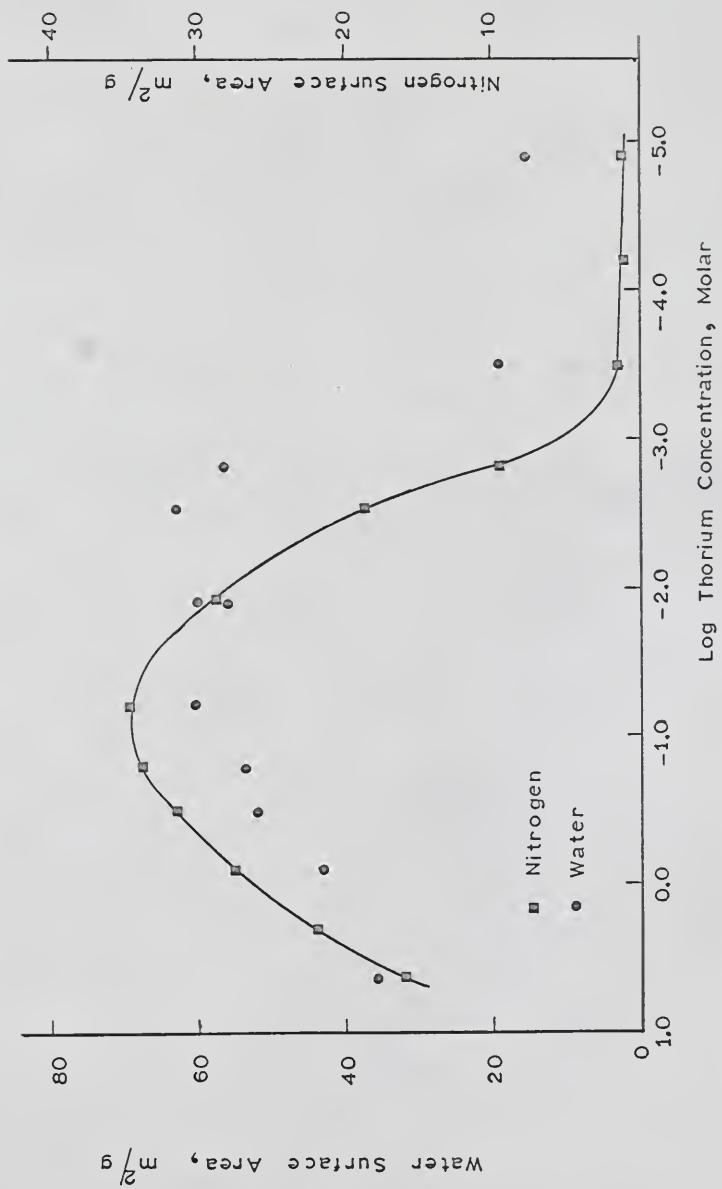


Fig. 8.-Plot of the nitrogen and water surface area vs. thorium concentration for catalyst series 9.

precipitated by the same procedure and washed with the same amount of water. It is apparent that there is an optimum thorium concentration at approximately 0.3-0.45 molar. There was a variable here other than the thorium concentration and that was the volume of thorium solution precipitated. It was not practical to precipitate as large a volume of the concentrated solution as was used for the dilute solutions due to the amount of thoria involved. Thus the speed and efficiency of stirring, and hence the rate of precipitation, probably played a role in determining the thorium concentration which produced the maximum surface area material. The figure also shows a plot of the water B.E.T. surface area versus thorium concentration; these results will be discussed later.

The effect that the amount of excess ammonium hydroxide, used for the rapid precipitation, has on the surface area is evident from Figure 9. A slight excess produces a low surface area material, and as the amount of ammonium hydroxide is increased the surface area rapidly increases and reaches a maximum value; the addition of a larger excess of base does not increase the surface area. The catalysts were all washed until peptization began; the larger quantities of base used for the precipitation required a greater amount of wash water to reach this point.

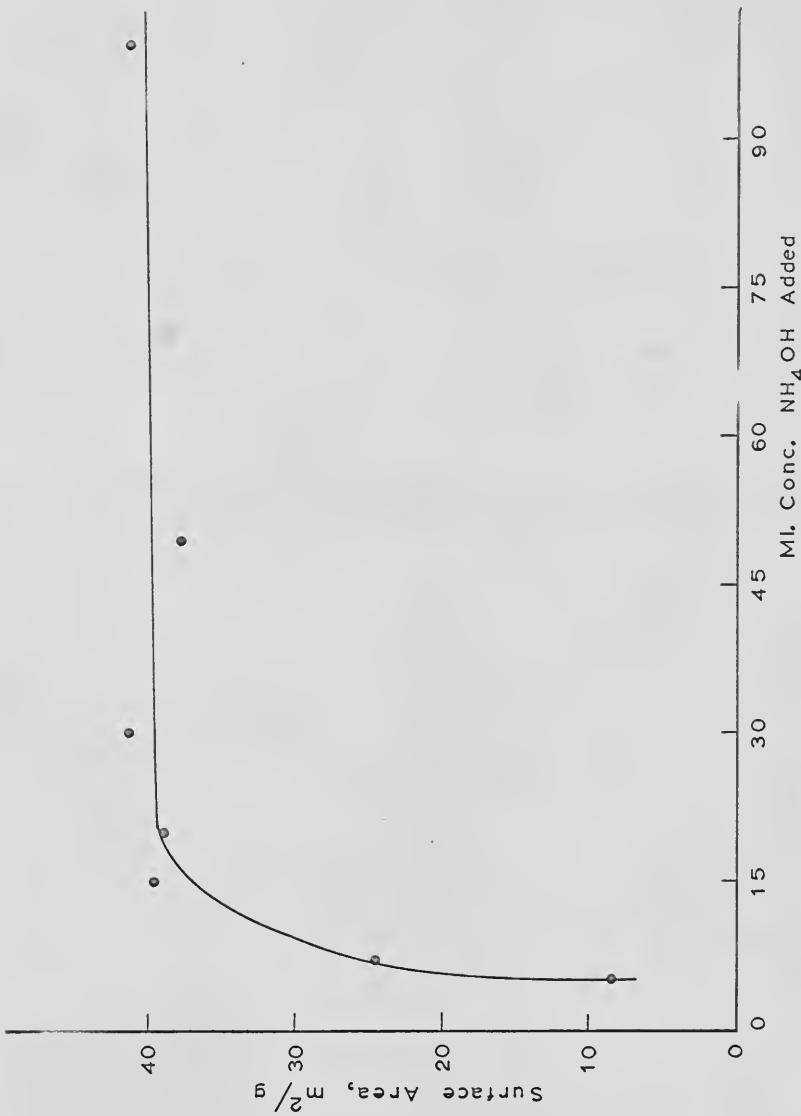


Fig. 9.—Plot of nitrogen surface area *vs.* amount of ammonium hydroxide added to standard amount of thorium solution to prepare catalyst series II.

Catalysts 16 and 17 show the effect of addition of base to produce a stoichiometry of Th(OH)_n with n between 3.16 and 4.60. It is noted that the addition of enough base for n to have a value greater than 3.28 caused complete thoria precipitation; with the exception of 17-A, 17-B, and 17-L the resulting oxides had a surface area less than 1.0 m^2/g . Even when 1.14 times the theoretical amount of base required to form Th(OH)_4 was dumped into the solution, the low surface area resulted.

From what was learned about preparation of high surface area thoria in the experiments described thus far one should have expected 17-A to have a low surface area since the ammonium hydroxide was added slowly. Instead, a higher surface area catalyst was obtained than for any of the previous preparations. The result for catalyst 17-B was even more surprising; the only difference between this catalyst and 17-A was that all quantities of reagents were halved. The surface area for 17-B was only about two-thirds the area obtained for 17-A.

Both 17-K and 17-L should have had a low surface area if, as indicated by the other catalysts of this series, the addition of enough base to give the stoichiometry with $n = 3.29$ is sufficient to cause low surface material to be formed. However, when 17-L was washed after collection by filtration, the precipitate peptized to such an extent that

it could not be recovered by filtration. Thus the solid was recovered by evaporation of the water at 110°C and, as will be discussed later, this was probably the reason for the high surface area.

A phenomenon that was noted with the slow precipitation method was a large increase in viscosity as the base was added to the thorium solution. The viscosity did not increase noticeably before incipient precipitation was reached. Even in the initial stage of precipitation the viscosity did not increase rapidly. As the precipitation continued the viscosity increased as might be expected. However, if one continued to add base to the stirred solution beyond the amount required for complete precipitation, a point was reached where the viscosity rapidly increased and, even with stirring, the mixture appeared to set as a gel. Either continued stirring or the addition of more base caused the viscosity to decrease. This increase was also observed for the rapid precipitation but was not as pronounced except for the very concentrated thorium solutions.

It was felt that a catalyst prepared from this thick gel should have a large surface area. Several catalysts were prepared from the thick gel obtained by precipitating at various rates and from solutions with a wide range of thorium concentrations. The point at which the thickest gel formed was difficult to detect since it was only determined

by ease of stirring and by its appearance. It appeared to require relatively less base for the more concentrated thorium solutions. With the exception of two catalysts, none of the catalysts prepared by adding base to thick gel formation, washing, and then drying the gel had a surface area greater than $5 \text{ m}^2/\text{g}$. As learned by catalyst series 21, these two exceptions were undoubtedly due to stopping the NH_4OH addition before thickest gel formation.

Gore and Dhar (65) observed and measured the viscosity of dilute thorium chloride solutions which had been subjected to hot dialysis to remove the chloride counter-ions. They concluded that since the viscosity increased steadily with purity (that is, as more and more Cl^- was removed by dialysis) the viscosity increase is related to the decrease in electric charge.

Another interesting, but unexplained, phenomenon was the spontaneous explosion of the thoria particles. As the solid was cooled to room temperature after drying at 100-110°C the particles would spontaneously explode. Cooling after activation at 600°C under vacuum did not cause much of this explosion. However, if the solid was ground even after standing for a few weeks the explosion of particles would continue for several minutes after grinding was discontinued. Shaking the material while sieving was sufficient to

initiate the spontaneous explosions which would continue for several minutes.

The effect of the activation atmosphere was determined using catalyst series 12 and the results are presented in Figure 10. The materials activated under vacuum yield the highest surface material up to temperatures above 700°C; above this temperature the surface was so small no conclusions could be reached. The activations in air and water vapor do not seem to follow a general trend. The activation in water vapor, except for the 500°C activation, seems to follow the trend of the vacuum activation. One would suspect that the surface area of the catalysts activated in water vapor would be smaller than the ones activated at the same temperature in air if water is the only material that causes the lower surface area for these activations. This is the case at 400° and 700°C but at 500° and 600°C the surface area is higher for the material activated under water vapor.

The effect of aging the hydrous thorium oxide after drying at 100°C is shown by catalyst 12. This catalyst hydroxide was prepared in June, 1963. Catalyst 12-A was obtained by activating some of this hydroxide at 600°C under vacuum for four hours a few days after precipitation. Some of this same hydroxide was stored in a closed bottle for 19 months and then activated at 600°C for four hours under vacuum. The surface area of the material activated shortly

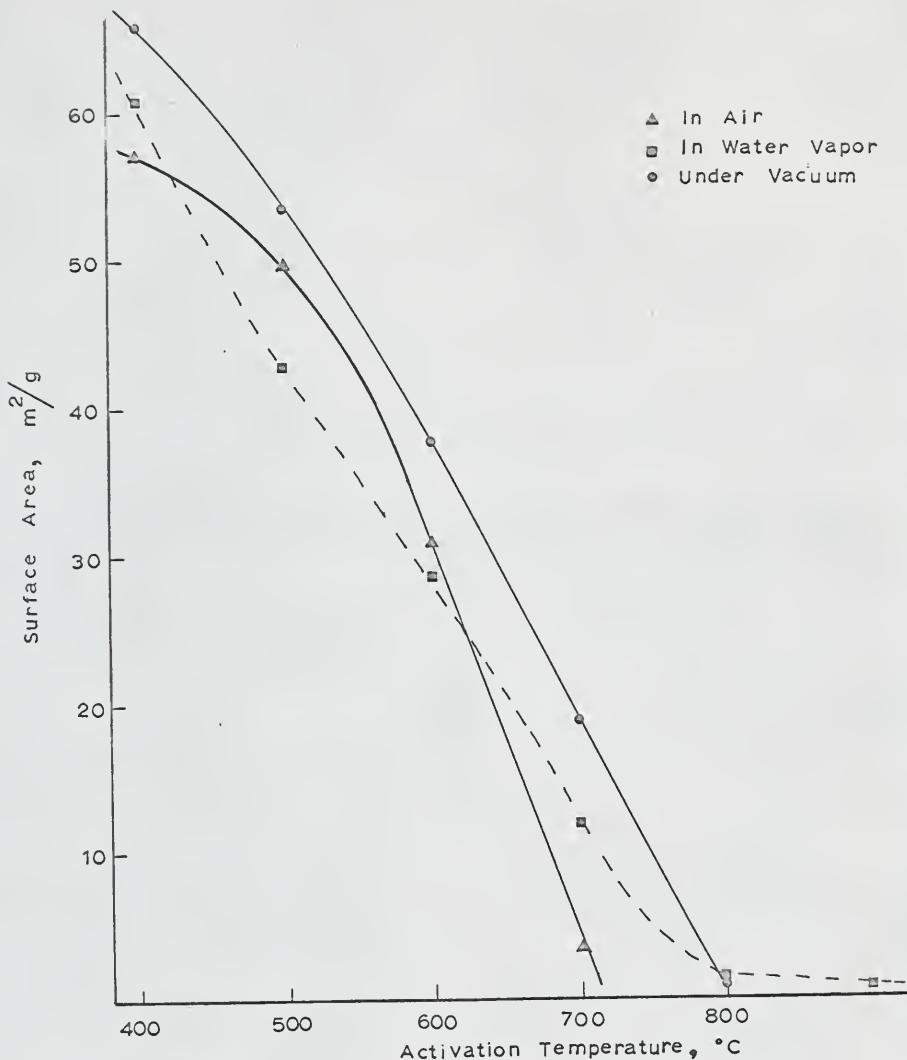


Fig. 10.-Effect of activation conditions on thorium oxide surface area.

after precipitation was $37.8 \text{ m}^2/\text{g}$ compared to $27.8 \text{ m}^2/\text{g}$ for the material activated 19 months later. However, the crystallite size as determined by X-ray line broadening did not increase by a measurable amount.

The effect of precipitating the hydroxide from a heated thorium nitrate solution was not investigated very thoroughly. Catalyst 9-J was precipitated from a nitrate solution at 70°C and the surface area of the material obtained was $25.2 \text{ m}^2/\text{g}$ as compared to $28.6 \text{ m}^2/\text{g}$ for the catalyst prepared with the same conditions at room temperature. 9-I was prepared by the same procedure but was heated at 70°C for one hour after precipitation. It would appear that heating in excess base increases the surface area only slightly; precipitation from a solution at 70°C slightly decreases the surface area. The effect of precipitation by slowly adding a thorium nitrate solution to a hot ammonium hydroxide solution (containing enough base to give $n = 4.60$) is demonstrated by catalyst series 20. These catalysts were washed with a solution of 15 ml concentrated NH_4OH per liter instead of with water. The surface area of the one precipitated at room temperature is seen to be $12.1 \text{ m}^2/\text{g}$; using the same amount of base for catalyst series 16 yielded materials whose surface area was less than $0.5 \text{ m}^2/\text{g}$. Heating at 80°C did not appear to affect the surface area of the material; however boiling the precipitation mixture doubled the surface area of the activated material.

The effect of slowly adding smaller amounts of ammonium hydroxide than required for precipitation to begin and then completing the precipitation by dumping excess concentrated ammonium hydroxide into the solution is shown by catalyst 10 series. The molarity of the stock solution was 0.18 M and compared to catalyst series 9 one should expect the surface area of a rapidly precipitated catalyst of this concentration to be about $30 \text{ m}^2/\text{g}$. Thus it would appear that the slow addition of ca. 10 per cent and 20 per cent of the theoretical amount of base required to form Th(OH)_4 has little, if any, affect on the final surface area. However, the slow addition of ca. 0.45 per cent of theory began to reduce the area obtained and the slow addition of ca. 0.65 per cent theory had reduced the area to one-third of the expected value.

The effect of the final pH of the mixture for the precipitation of both thorium nitrate and thorium chloride solutions is presented in Figure 11, and is seen to depend on the anion which is present. The Cl^- ion apparently is not able to stabilize the soluble thoria species as well as the nitrate ion as evidenced by the formation of a precipitate at a lower pH value. The maximum area obtained from the chloride is less than half the maximum area for the nitrate. The conditions for maximum area for the chloride catalyst were not determined; thus it may be possible that

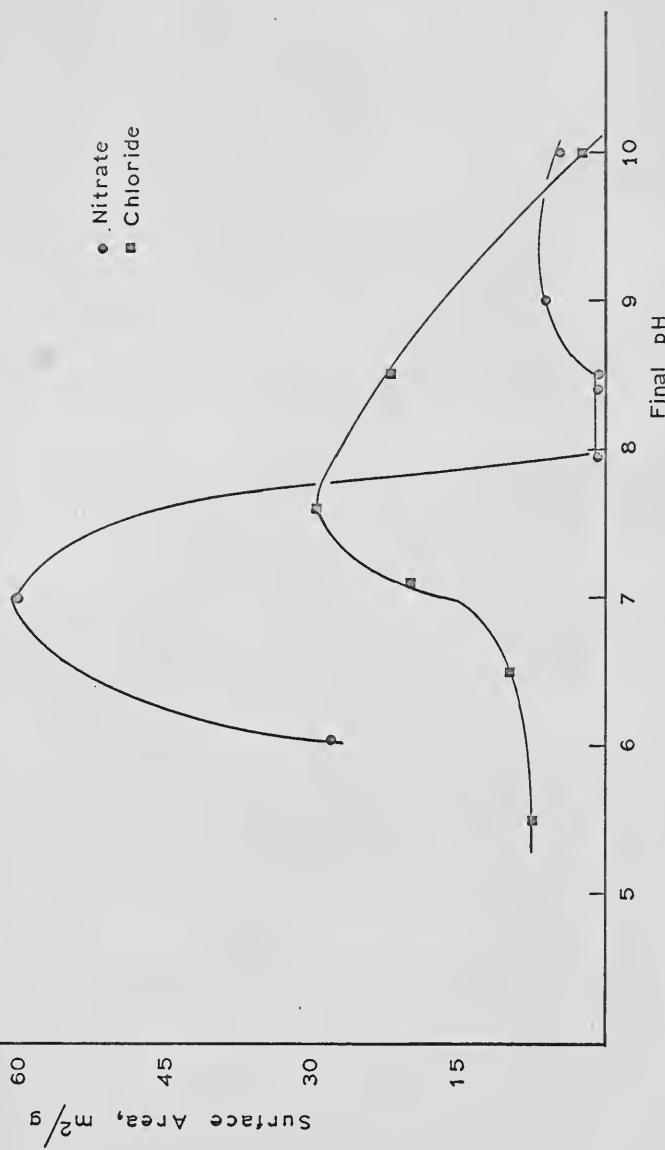


Fig. 11.-Effect of final pH of thorium solution on the oxide surface area.

higher surface area catalysts can be obtained for the chloride solution than the ones presented here. Also apparent is the fact that the surface area obtained is not nearly so pH dependent for the precipitation from the chloride solution as from the nitrate solution.

The maximum surface for the material from the chloride seems to occur at a pH 7.5-7.8 whereas the maximum for the nitrate would appear to occur at about pH 7.0. The surface area for the material from the nitrate solution decreases from its maximum value of greater than $60 \text{ m}^2/\text{g}$ to less than $1 \text{ m}^2/\text{g}$ at a pH of 7.9. As the pH is increased to ca. 8.5 the surface area remains less than $1 \text{ m}^2/\text{g}$; then as the pH is made more basic the material obtained has a pH of ca. $6 \text{ m}^2/\text{g}$ at pH 9. Increasing the pH from 5.5 to ca. 7.5 for the chloride solution causes an increase in the surface area of the material obtained, then a further increase in pH causes a gradual decrease in surface area until at a pH 10 the surface area is ca. $1 \text{ m}^2/\text{g}$.

One explanation for the two peaks in the surface area pH curve for the nitrate solution is that they are caused by the charge of the material. By electrophoresis studies Thomas and Kremer (66) found the particles of solutions prepared by dialysis of the hydrous oxides were positively charged due to Th^{+4} or H^+ ion adsorption; the pH of these solutions was ca. 4.0. These authors found that if a salt,

containing hydroxyl groups, for example, potassium tartrate, was added to the solutions precipitation occurred followed by redispersion upon addition of more of the salt solution. The thoria particles after redispersion were found to be negatively charged. Organic anions not having the hydroxyl group did not cause charge reversal. Thus the high surface obtained at pH ca. 7.0 could be viewed as being formed from these positively charged particles; the repulsive charges would cause the gel to be of a more porous nature. As the pH is increased the gel charge decreases and the gel structure becomes more compact. Finally, as the pH is further increased the gel becomes negatively charged and the gel again becomes porous and the surface area becomes measurable again. According to Anderson (43), the Cl⁻ ion is much more strongly adsorbed than the nitrate. These more strongly adsorbed or complexed Cl⁻ would require a higher OH concentration before they are replaced. Thus it is suspected that the broad maximum for the pH surface area curve for the chloride solution corresponds to merely the first peak of the curve for the nitrate solution. The olation process will be discussed more thoroughly after considering the preparation of catalysts from a colloidal solution.

F. Preparation of Catalysts from Colloidal Thoria

The highest surface area catalysts were obtained by precipitating a colloidal thoria dispersion. The preparation of a colloidal thoria dispersion appears to be as dependent on the conditions as the preparation of the hydroxide. For catalyst 23 series two hydroxides, one precipitated slowly and one precipitated rapidly, were heated in water and at least half of the hydroxide dissolved after only two hours heating at 90°C. Neither of these two solids was washed before drying at 100°C. A hydroxide, rapidly precipitated, washed six times with 200 ml of water each time, and dried at 100°C, would not dissolve to any appreciable extent even after boiling for 24 hours. The addition of approximately six grams of thorium nitrate hydrate in small portions to the boiling mixture produced a water clear solution. The hydroxide for catalyst 30, after drying at 100°C without being washed, contained too much NH_4NO_3 to dry completely. The solid was dissolved in water and reprecipitated; this precipitate was washed once with 400 ml water. Most of this sample did not dissolve even after boiling for 48 hours. Thirty ml of 0.66 M thorium nitrate solution was added to the boiling solution over a three day period and nearly all of the solid material dissolved. This solution had a milky appearance and was a pale blue. Previous colloidal thoria samples have been reported to be water clear (37), slightly opaque (38), or yellow-orange (9).

The first catalysts prepared from a colloidal solution were series 23. The hydroxide which was used to prepare the samples 23-C and 23-E was activated at 600°C and the material produced a surface area of less than $1 \text{ m}^2/\text{g}$. After this hydroxide had been heated in water at 90° for two hours the insoluble solid had a surface area of 80.0 m^2/g . When the pH of a similar mixture was adjusted to 7.0 before collecting the solid the surface area increased to 90.6 m^2/g . This higher surface area was probably due to a mixture of material with a surface $80 \text{ m}^2/\text{g}$ described above and a higher surface area material as described in catalyst series 21. No significant difference was noted whether the original hydroxide was precipitated slowly or rapidly.

The colloidal material for series 21 was prepared from a hydroxide which itself had been precipitated from a colloidal material. The hydroxide used to prepare the second colloidal dispersion had a surface area of 90.0 m^2/g after activation at 600°C. This time, after boiling the suspension for three hours, the undissolved solid had lost surface area from $90 \text{ m}^2/\text{g}$ to $69.5 \text{ m}^2/\text{g}$ instead of increasing in surface area. Ammonium hydroxide was added to the filtrate after collecting the above solid until the pH was 7.4. The surface area of this material after activation at 600°C was $110 \text{ m}^2/\text{g}$. Two duplicate samples agreed quite well with these; the insoluble material had a surface area of $69.6 \text{ m}^2/\text{g}$.

and the material from the filtrate had a surface area of 114 m^2/g . A solid obtained by adjusting the pH of the mixture without separating the solid has a surface area of 78.6 m^2/g , indicating that this material was a mixture of the low and high surface area material described above. This would indicate that the material prepared by Rombau and Peltier's patented method using the precipitated hydroxide was a mixture of catalytic materials.

The effect of pH seems to depend, at least to some extent, on the colloidal dispersion being precipitated. For the series 21, a final pH of 7.0 yielded the highest surface area material obtained to date. For catalyst series 26 a pH of 8.5 gave the highest surface area material; however, the samples precipitated at lower pH dissolved when drying at 100°C. For catalyst series 30, the highest surface area material was obtained at a pH ca. 9.5; the surface area of the material for which the final pH was 7.0 was very low. The material prepared by dumping 100 ml concentrated base into the colloidal dispersion had nearly as large an area as the highest area material obtained; that is, 74.0 m^2/g as compared to 79.5 m^2/g for the final pH of 9.5. Catalyst series 21 was prepared before it was noted that higher surface areas are obtained at a pH greater than 7; hence it might have been possible to obtain a higher area than 114 m^2/g if a higher pH had been used.

It also appears that the initial pH of the colloidal solution which is precipitated has an effect on the surface area obtained. For 21-O and 21-P the initial pH for the last precipitation was 3.7 and 4.0, respectively. The catalysts prepared by these precipitations had a surface area of 110 and $114 \text{ m}^2/\text{g}$, respectively. However, the dispersion for catalyst series 30 had an initial pH of 1.8 and the material precipitated to a final pH nearly the same as the two 21 series catalysts described above had a surface area of $5 \text{ m}^2/\text{g}$.

The insoluble material for series 30 was quite different compared to both series 21 and 23. The surface area of this solid for the series 30 material was less than $1 \text{ m}^2/\text{g}$. This low area may be due to the low pH of the colloidal dispersion in contact with this solid.

The attempt to prepare a colloidal solution from the washed thorium hydroxide obtained from a thorium chloride solution after drying at 100°C was unsuccessful even after boiling for 24 hours. A thorium chloride solution was slowly added over a period of time to the boiling mixture until about 80 per cent as much Th had been added as was present as the solid. No noticeable amount of solid was dissolved by this treatment. However, it is noted that the area of the catalyst prepared from the supernatant liquid by precipitation at a pH of 7.5 was about 1.3 times larger than obtained at a similar pH from an ordinary thorium chloride solution.

It might be appropriate at this time to compare these surface areas with those of other common catalytic materials. Areas for aluminas activated at 600°C are commonly reported in the neighborhood of $400 \text{ m}^2/\text{g}$ and silica gel activated at 600°C is not much greater than $425 \text{ m}^2/\text{g}$. Thus on a weight basis thoria does not compare very favorably. However, the density of precipitated thoria is reported to be approximately 10.6 g/ml while the density of quartz is reported to be 2.66 g/ml and alumina to be ca. 3.7 g/ml. Then the surface areas are $1210 \text{ m}^2/\text{ml}$ for thoria, $1100 \text{ m}^2/\text{ml}$ for silica, and $1480 \text{ m}^2/\text{ml}$ for alumina. Even if one uses the lower value of 8.5 g/ml for precipitated thoria density, the surface area of thoria still compares favorably with the areas of silica and alumina on an area/volume basis.

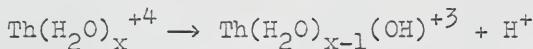
The motivation for studying almost exclusively the precipitation from a nitrate solution by ammonium hydroxide should also be explained. One would like to use a single component catalyst since a mixed oxide catalyst adds more variables to an already complex structure. This desire then eliminates the use of the metallic hydroxides since these metal ions will be adsorbed during the precipitation and will thus remain incorporated in the solid after activation. Likewise, the anion should be one which will not remain after activation. The use of ammonium hydroxide and thorium nitrate leads to the formation of ammonium nitrate which,

when heated to the activation temperature used in this study, will decompose to oxides of nitrogen and water. These nitrogen oxides are not adsorbed in a detectable amount at the higher activation temperatures (25). The other decomposition product, water, is already present.

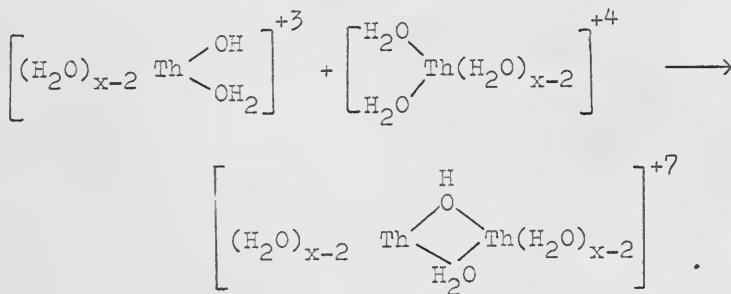
G. Discussion of a Possible Reaction Path for the Precipitation of Thoria

The solution chemistry of thoria is very complex, as was evident by the contradiction among the various authors' work described in the discussion section. Indeed, Hentz and Tyree (41), when discussing the nature and structure of the species present at increasing OH^- concentration, state "..., but the validity of this theory and the general nature of this phenomenon are subject to the results of considerable further work along these lines." If the assignment of the equilibrium species in a thorium solution is not definite at this time, even a schematic outline of the path of the precipitation process must be speculation within the framework of scant knowledge of thorium, and ions which should behave similarly, in solution. Then the following description of the precipitation is presented as a means of summarizing the surface area of the materials obtained and a model for obtaining new ideas for catalyst preparation, especially colloidal thoria preparation.

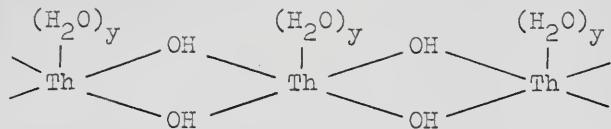
Nearly all authors are in agreement that the thorium is present in acidic or even dilute aqueous solutions as the hydrated Th^{+4} ion. This solution is acidic because of olation, that is, the formation of an OH^- group from one of the coordinated water molecules with the simultaneous formation of an H^+ ion, such as



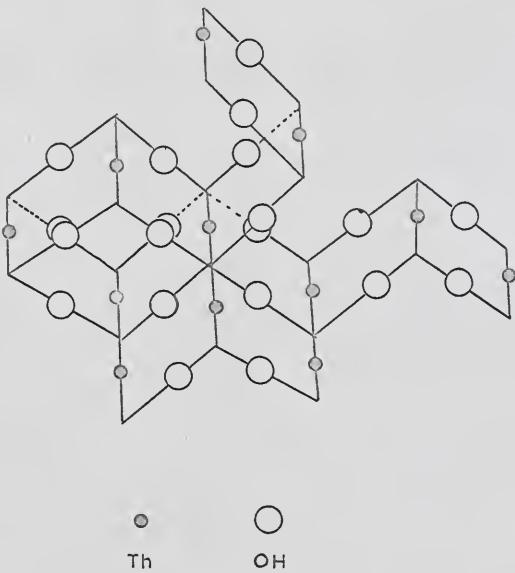
Since the solutions are dilute and the NO_3^- ion is not strongly coordinated, few of these thorium atoms will be coordinated with nitrate ions. As base is added more olation occurs. This olation not only produces more H^+ , it also reduces the charge of the hydrated thorium ion. As the concentration of the olated species is increased dimerization of two such complexes could occur, for example,



As more and more olation occurs it is not difficult to visualize the formation of species such as postulated by authors referred to in the discussion section, for example,



This is just the structure advanced by Lundgren and Sillen (32) for the $(\text{Th}(\text{OH})_2)_n^{+2}$ chains with y water of hydration arranged in some order around the metal ion. Now as more base is added solation of some of the remaining water of hydration can occur. This then allows branched chains to form and the formation of a three-dimensional network as depicted below.



The water of hydration has not been drawn in this sketch for the sake of clarity. Now it is noted that each ol group occupies the same geometrical arrangement about thorium atoms as oxygen atoms occupy in crystalline thorium dioxide. Then as more base is added the familiar oxolation process, that is, the conversion of ol groups to bridging oxo groups, leads to a hydrated thorium oxide structure. The structure drawn is an idealized structure; in reality one would expect voids due to missing $\text{Th}(\text{OH})_2$ groups and the incorporation of impurity NO_3^- and NH_4^+ ions in the structure. Also, olation to form a three-dimensional lattice and oxolation probably occur simultaneously as this reduces the net charge of the structure formed. However, one would expect a rather well ordered structure for the agglomerates formed. A well ordered structure would then yield a solid whose surface is nearly the geometrical surface of the particle and this is on the order of cm^2/g .

Now as the thorium solution is made more concentrated the increased nitrate ion concentration would cause more and more of this ion to penetrate the thorium hydration sphere. Larsen and Brown (34) proposed each thorium is coordinated to two bidentate nitrate ions. This nitrate ion would also be expected to be present in the chain found by olation.

One structure of $\text{Th}(\text{OH})_2(\text{NO}_3)_2$ with a chain configuration which has the basic chain structure found by Lundgren

and Sillen (32) and which has each thorium surrounded by eight oxygen atoms is shown in Figure 12.

The nitrate ions in the coordination sphere have accomplished two things; they have neutralized the two positive charges on each thorium atom and they have eliminated the possibility of forming a three-dimensional structure as was the case when water molecules completed the coordination sphere. Now as the pH is increased oxolation can take place and one can visualize two things happening; the OH^- groups replacing some of the nitrate groups as well as causing the soluble chains to become insoluble. The OH^- groups which replace nitrate groups can form ol bridges with other chains which then undergo oxolation. However, the nitrate groups prevent the close packing of these two chains and it is possible to form a very open network of these chains with each chain randomly attached at points along its length to other chains whose length is randomly orientated to the other chain lengths.

If the pH is slowly increased the replacement of NO_3^- ions by OH^- can take place before the precipitation pH is reached and more and more olation and oxolation can occur to produce a close packed structure. The precipitated material would have a compact structure and a low surface area after activation. However, if the base is added rapidly one would expect the precipitation pH to be reached

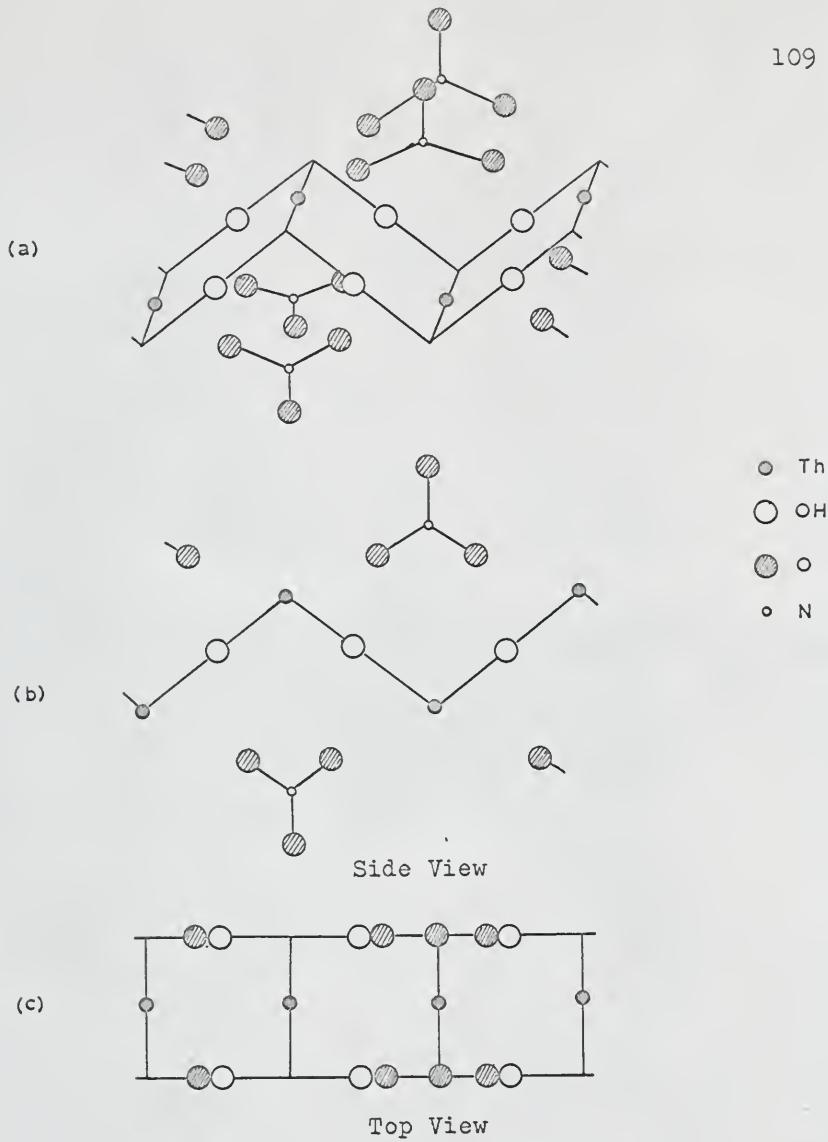


Fig. 12.-Possible structure of $[\text{Th}(\text{OH})_2(\text{NO}_3)_2]_n$.

before very long chains would have time to form and it would be these shorter chains which are precipitated; also the rapid precipitation causes the porous gel structure to form so rapidly that many of the coordinated nitrate groups would be trapped in the gel structure.

One would expect, if the precipitation proceeds as in the last paragraph, the unwashed, rapidly precipitated material to have the highest surface area. However, the precipitation process causes much of the ammonium nitrate formed to be trapped in the gel structure. Pure ammonium nitrate melts at 160°C and decomposes at about 210°C. There is sufficient ammonium nitrate present in the unwashed precipitate that when the activation is done under vacuum some ammonium nitrate distills from the solid and condenses in the activation tube just above the furnace. If some of the ammonium nitrate present in the solid were to melt and "wet" the gel before decomposition one would expect both the "wetting" of the surface and the later exothermic decomposition of the ammonium nitrate to sinter the porous hydrous oxide structure. Thus it is felt that the major effect of the early washing is the removal of this trapped ammonium nitrate and hence a rapid increase in the surface area with washing. However, the washing also causes some of the coordinated nitrate to be replaced by ol or oxo groups and this causes a decrease in the surface area finally obtained.

Hence the maximum in the surface area versus washing curve and the gradual loss in surface area with increased washing beyond that for maximum area.

The colloidal catalyst preparation can also be interpreted using this chain structure. The reversal of oxolation is slow and usually requires much more drastic treatment than the oxolation process (67). As noted in the preparation of catalyst 26-A the washed precipitate could not be put into solution by boiling in water. However, by increasing the nitrate concentration by adding thorium nitrate one causes penetration of some nitrate ions into the oxolated structure. This process causes the larger agglomerates to form several smaller particles; however, not enough nitrate is added to lower the pH and to increase the nitrate ion concentration sufficiently to cause the destruction of the smaller particles. Now reprecipitation by adding base causes these larger particles to be precipitated by being randomly joined together. There should be many voids in between these precipitated particles. Then, in order to keep this porous structure, one would want to form oxo bridges where one particle is joined to another, hence a higher pH should be required for a maximum surface area in this case than in the precipitation process.

Obviously the preceding structures have been the idealized situation; in actual practice one would not expect

to have a chain composed of repeated $\text{Th}(\text{OH})_2(\text{NO}_2)_2$ groups but a chain composed of unit groups with varying stoichiometry. The true situation would probably be somewhere between these two extremes. The variation in physical properties would be determined by how closely the intermediate path came to the idealized situation.

H. Precipitation of Thoria from a Mixed Solvent System

Catalyst series 24 shows the effect of precipitation from a mixed solvent system. For the water-isopropanol solvent mixture, dilution probably was affecting the surface area as well as the decreasing percentage of water in the solvent. If the alcohol were to replace many of the NO_3^- ions as ligands in a chain structure, such as advanced to explain the precipitation, then the chain structure would be surrounded to a certain extent by a hydrophobic film of organic methyl groups. This could prevent to a large extent cross linking of the chains even after precipitation by the addition of the base. Then as one washes the precipitate the alcohol is replaced by water molecules which can form ol or oxo bridges much in the manner the nitrate ions could be replaced in the preceding discussions.

At this time it might be advisable to caution readers that the catalyst preparation procedures described in Chapter IV should not be considered to be a recipe. In the preparation of a catalyst the experimental technique, or art,

will affect the final results. Thus one should not feel free to increase the amounts of all materials given for one of the preparations tenfold and expect to obtain the same final surface areas. However, one should be able to prepare a catalyst having the desired surface area with the use of much less art if the general guidelines found from this study are followed.

More reproducible results are obtained using some of the preparative methods than with other ones. The thermal decomposition of washed thorium oxalate yielded thoria with a nitrogen B.E.T. surface area of approximately $15 \text{ m}^2/\text{g}$ and is quite reproducible. The rapid thermal decomposition of thorium oxalate containing nitrate ions appeared to be reproducible. The most reproducible precipitation condition, yielding thoria with an area ca. $45 \text{ m}^2/\text{g}$, was found to be the following: use a thorium nitrate solution that is ca. 0.45 M; use three to five times the theoretical amount of concentrated ammonium hydroxide required to form Th(OH)_4 ; precipitate by dumping the base into the rapidly stirred thorium solution; wash by repeatedly slurring the precipitate with the wash water and filtering, using a total of approximately 25-35 ml water per g $\text{Th(NO}_3)_4$. One of the above three procedures would be recommended for the initial experiments if one was undertaking a study of catalytic reactions over thoria. Also the thoria obtained by the

precipitation from a single colloidal thoria dispersion is quite reproducible; however the preparation of reproducible dispersions is much more difficult.

I. Average Crystallite Size from X-Ray Line Broadening

The average crystallite size was determined from the X-ray line width using the Scherrer equation. This method is discussed at length by Klug and Alexander (59) and references are given to even more complete discussions of specific topics. According to these authors this method of calculation yields satisfactory values of the relative sizes for samples belonging to a related series even though the premises upon which the formula rests result in considerable uncertainty as to the absolute sizes.

As shown by McBride et al. (23) the surface area for a material with no pores should vary inversely with crystallite size. The plot of log surface area versus crystallite size for catalysts series 7, 12, and 25 (Figure 13), shows that while the data points may fit a straight line for high surface area materials they certainly do not even approximate a straight line for the entire range of surface areas.

A comparison of the surface areas and crystallite sizes for catalyst series 13 is interesting. The average crystallite size is 84.9 Å and only two of the seven catalysts vary from this average value by more than 0.6 Å. The surface area for these catalysts ranges from a low of

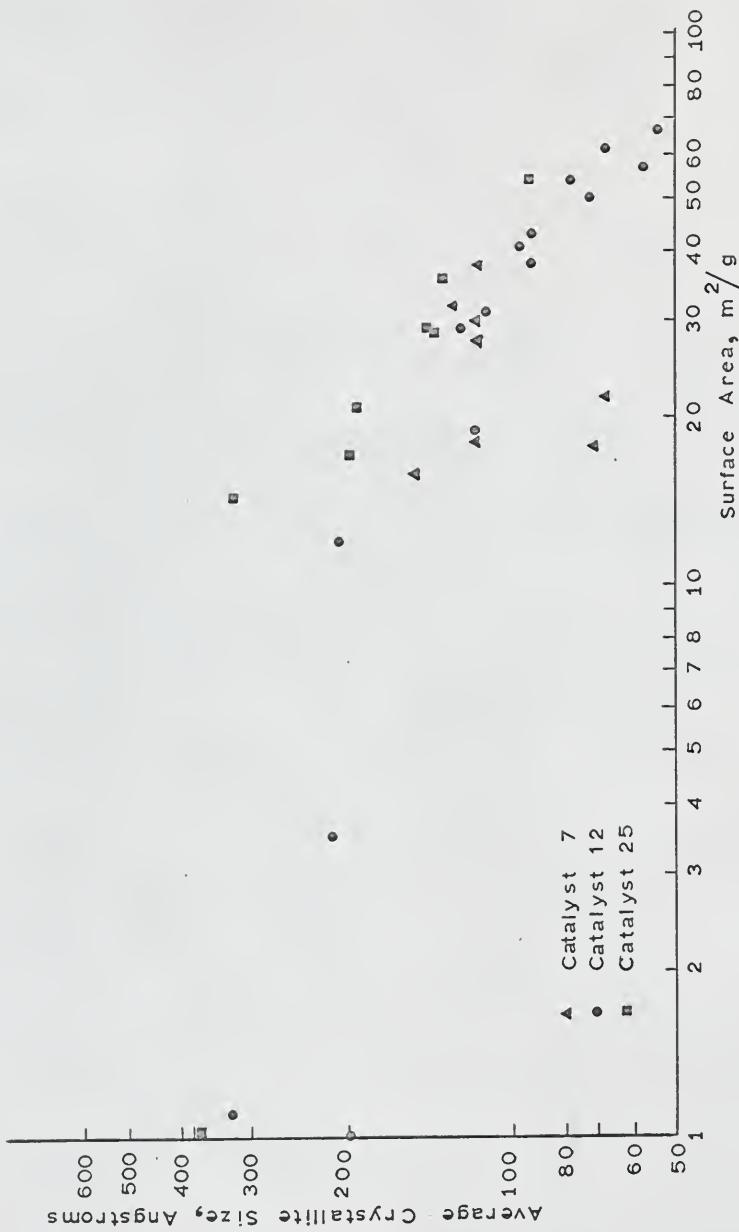


Fig. 13.-Plot of average crystallite size as determined by x-ray line broadening vs. surface area.

13.7 to a high of $38.8 \text{ m}^2/\text{g}$. An inspection of Table 2 will show that the great majority of the precipitated catalysts, excluding the colloidal preparation, which were activated for four hours at 600°C under vacuum have a crystallite size between 80 and 100 Å. For the 12 catalysts 4-A to 4-L the average crystallite size is 92.2 Å. Only three samples vary from this average by more than 4 Å and none of the samples vary by more than 9 Å from this average. Indeed, catalysts 4-M, 4-N, and 4-O were heated at 600°C for a total of between 50 and 75 hours and these crystallite sizes were still less than 10 Å larger than this average value. It should be pointed out that the table listing the crystallite sizes contains some catalysts whose preparation was not given in Chapter IV; these catalysts were all prepared by precipitation and activated at 600°C for four hours under vacuum.

Figure 14 shows that the activation temperature has an effect on the crystallite size. The crystallite size apparently increases slowly up to an activation temperature of 600°C ; above this temperature the increase in crystallite size becomes greater with temperature increases. Comparison of all the data on crystallite sizes for the precipitated catalysts indicates that the average crystallite size depends primarily on the activation temperature rather than on the variables of precipitation and washing.

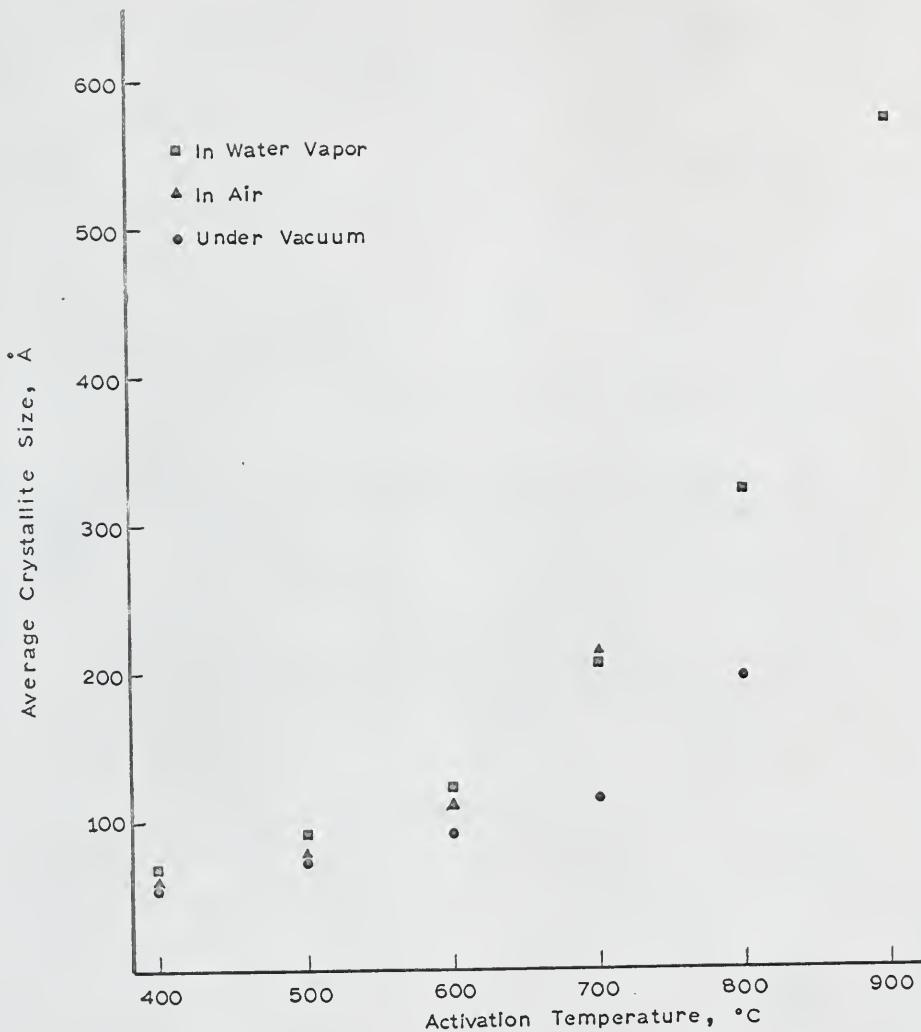


Fig. 14.—Effect of activation temperature on the average crystallite size for catalyst series 12.

Catalyst series 25, Figure 15, prepared by the thermal decomposition of thorium nitrate hydrate differs from the precipitated material in that it does fit the equation derived by McBride et al. (23) using a value of $1/F = 0.690$. Interpreting $1/F$ in the manner McBride et al. do would mean that 31 per cent of the crystallite's surface is unavailable for nitrogen adsorption during the B.E.T. area determination.

Figure 6 is a plot of the surface area versus average crystallite size for catalysts 7 and 21. There does seem to be a linear relationship between these two quantities for catalyst series 21, prepared by the colloidal method. However, doubling the surface area from 60 to $120 \text{ m}^2/\text{g}$ in this linear portion of the curve only causes enough decrease in crystallite size to account for a 1.25 increase in surface area. In addition, catalyst 21-P has a larger surface area than is calculated from the crystallite size even if all of the surface of every crystallite is accessible to nitrogen in the B.E.T. measurement. Also the data for catalyst 7 show that the crystallite size-surface area relationship could not hold for the oxalate catalysts prepared for this study. For the low area materials prepared either by a slow heating rate or from washed oxalate (shaded points) it is seen that the crystallite size varies from 71 to 150 \AA while the surface area is essentially constant. Also, for a crystallite size 116 \AA the areas varied from 18 to $37.4 \text{ m}^2/\text{g}$.

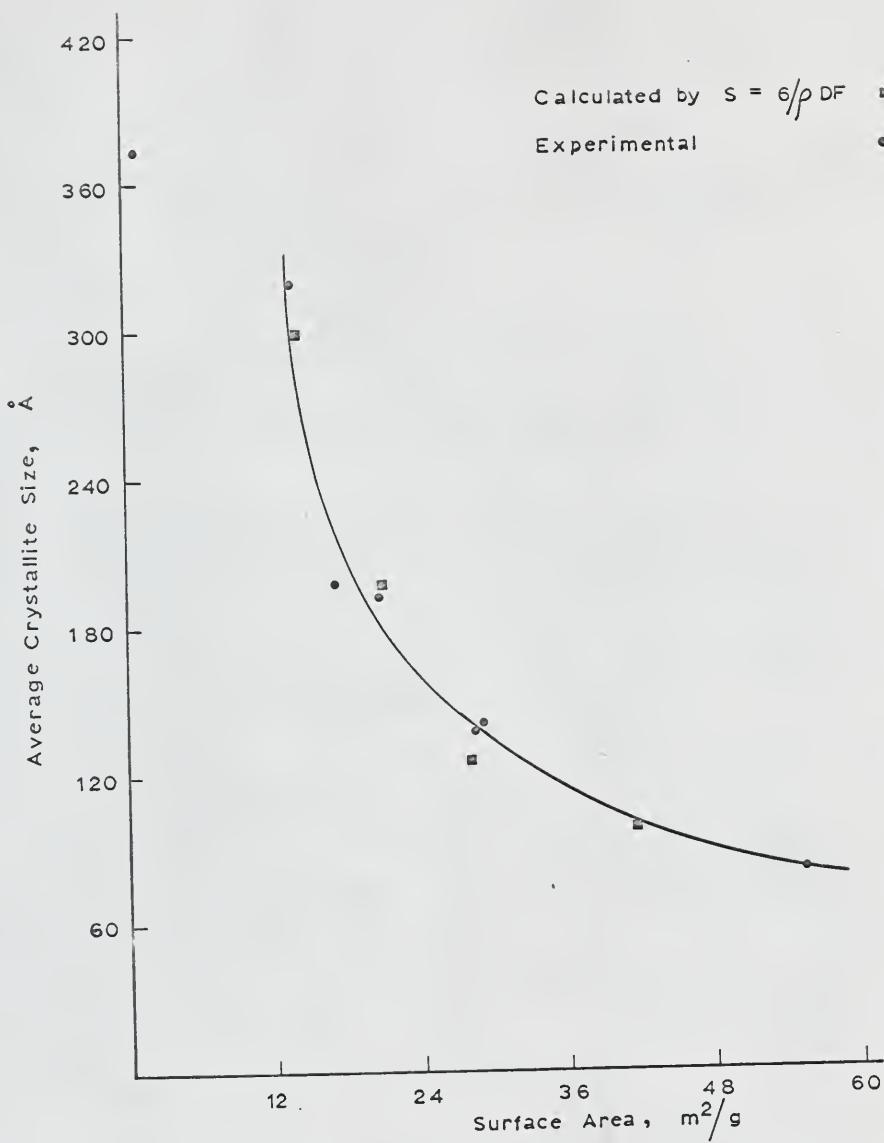


Fig. 15.—Plot of crystallite size vs. surface area for catalyst series 25.

The X-ray spectra for several catalysts from different preparations were run from $2\theta = 10^\circ$ to $2\theta = 60^\circ$. No lines were observed that corresponded to the expanded thoria structure. However, the spectra were obtained by scanning at a rate of $1/2^\circ/\text{minute}$ rather than by the photographic method used by some of the previous authors who had noted the expanded thoria structure.

J. Sintering of Thoria Catalysts

Another important property of a catalyst is the rate of loss of surface area during reaction runs and reactivation. Thus the loss of surface area for heating at 600°C for long periods of time was investigated. For the precipitated material the rate of loss of surface area is much more rapid for the first 10-20 hours of heating. After this period the rate of surface area loss becomes much less.

Figure 16 shows the effect of prolonged heating on the surface area. The catalysts 4-M, 4-N, and 4-O appear to decrease in surface area at nearly the same rate beyond the first 15 hour heating period. Catalyst 17-A shows a rapid initial loss of area; however, the loss of area after heating about 40 hours appears to be quite slow. Catalyst 23-F, with an even higher initial surface area, shows a high initial loss of area; however this loss has a smaller absolute magnitude than for 4-M, -N, -O and 17-A, and the loss/unit area/hour is much smaller for 17-A. Also the slow,

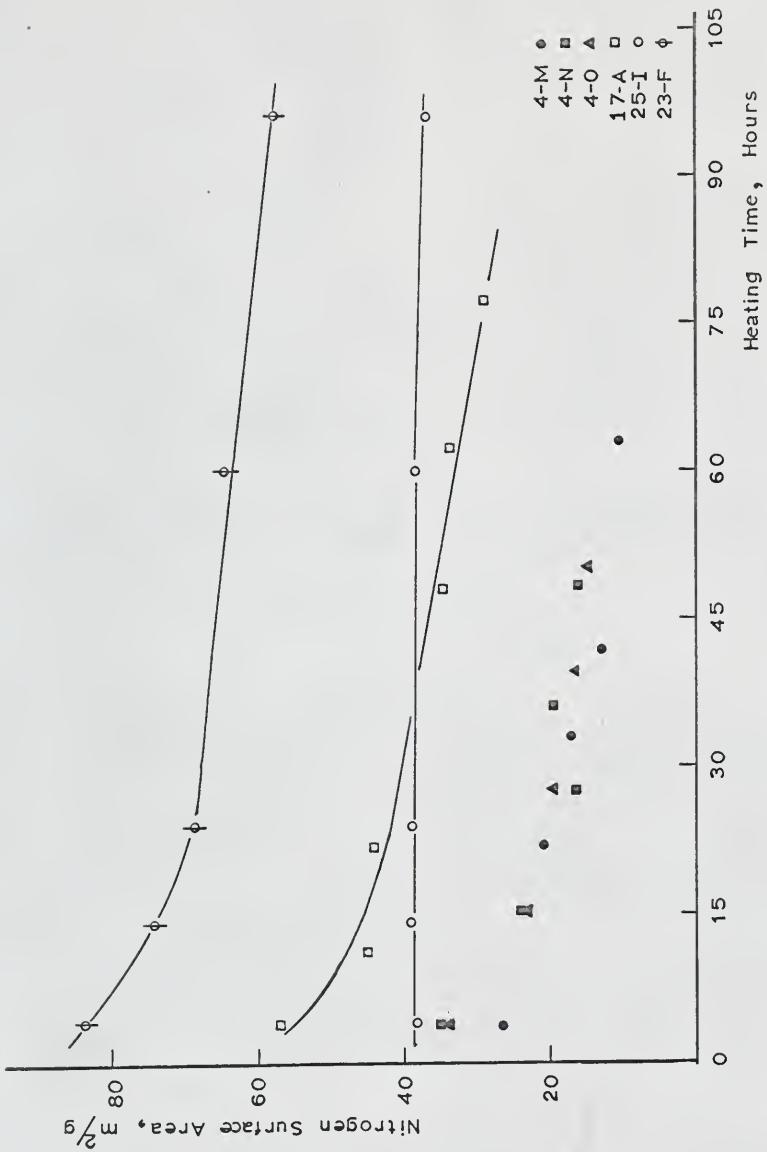


Fig. 16.—Effect of extended heating periods on the nitrogen B.E.T. surface area of thorium oxide.

nearly linear decrease of area with heating time seems to begin at about 20 hours heating time instead of about 40 hours as for 17-A.

The course of the sintering process for even simple particle shapes is still debatable. In view of the lack of knowledge about the thoria particle shapes and surface structure no discussion of the possible sintering processes will be undertaken.

Catalyst 25-I, prepared by the thermal decomposition of hydrous thorium nitrate, is quite different in that heating for a period of 96 hours results in only a decrease of area which is almost within the experimental error of the surface area measurement.

These losses of surface area during heating indicate that if one wishes to make a series of kinetic measurements over the precipitated thoria catalysts one should activate the catalyst for 20-35 hours at 600°C under vacuum. This would insure one of making the kinetic measurements on a catalyst whose surface area did not change appreciably during the measurements. However, this material after the long activation period would probably have different catalytic properties than the higher surface area material.

K. Water Adsorption on Thoria

One of the objectives of this investigation was to be a study of the n.m.r. line width of water adsorbed on

thoria from various preparation methods. Brey and Lawson (57) calculated the water monolayer coverage by using the surface area obtained by nitrogen. This requires one to assume that the water is only physically adsorbed and also assume a value for the area occupied by a water molecule. Heats of adsorption measurements (52) indicate that some water is chemisorbed; Neikam (6) found that it was necessary to assign different areas, σ^- , to a water molecule adsorbed on various aluminas to obtain agreement between monolayer values for the adsorption of nitrogen and water.

The adsorption isotherms for catalyst 4-L and 7-M give a type IV isotherm according to the Brunauer, Deming, Deming and Teller classification (49). This type isotherm is interpreted as being due to multilayer adsorption of the type that leads to a type II isotherm; however, for type IV there is a limited pore volume. For the precipitated catalysts the amount adsorbed at the saturation pressure increases with area but there is not a great difference in the amount adsorbed by a high area material compared to the low area material. However, the catalysts derived from the oxalate had a much larger adsorption capacity at the saturation pressure than the precipitated material had. The isotherm for catalyst 22-B and 22-C will be discussed more completely later in this section.

Three samples, 12-C, 14-E, and 17-A were preheated to 250° before measuring the water surface area; then

preheated again at 400°C and the water surface area re-determined. Two things are evident: first, the surface area for the lower preheating temperature is lower than for the higher preheating temperature, and second, the loss of surface area for these three catalysts preheated first at 250° and then at 400°C is much greater than for samples just preheated at 400°C. Indeed, the loss of surface area for the two preheatings is of the order of magnitude one would expect for heating at 600°C for a 10-15 hour period.

Apparently at the lower preheating temperature the water is removed much more slowly and thus has a greater opportunity to contribute to sintering and pore closure at this elevated temperature. The higher surface area obtained by preheating at 400°C is attributed to removal of more strongly adsorbed water or desorption of water by the destruction of two surface hydroxyl groups to water and an oxygen anion.

Plots of the nitrogen surface area versus the water surface area are presented in Figures 17, 18, and 19. The extension of the straight line does not pass through the origin. Neither is the slope of these lines equal to unity; the slopes are: thoria derived from oxalate, 1.77; series 11, 1.5; series 14, 1.43; and series 21, 2.2.

This large slope for the oxalate-derived samples could be explained by the fact that they are from essentially three types of catalyst preparations. The slope is determined mainly by the samples 7-I and 22-B and -C. Catalyst

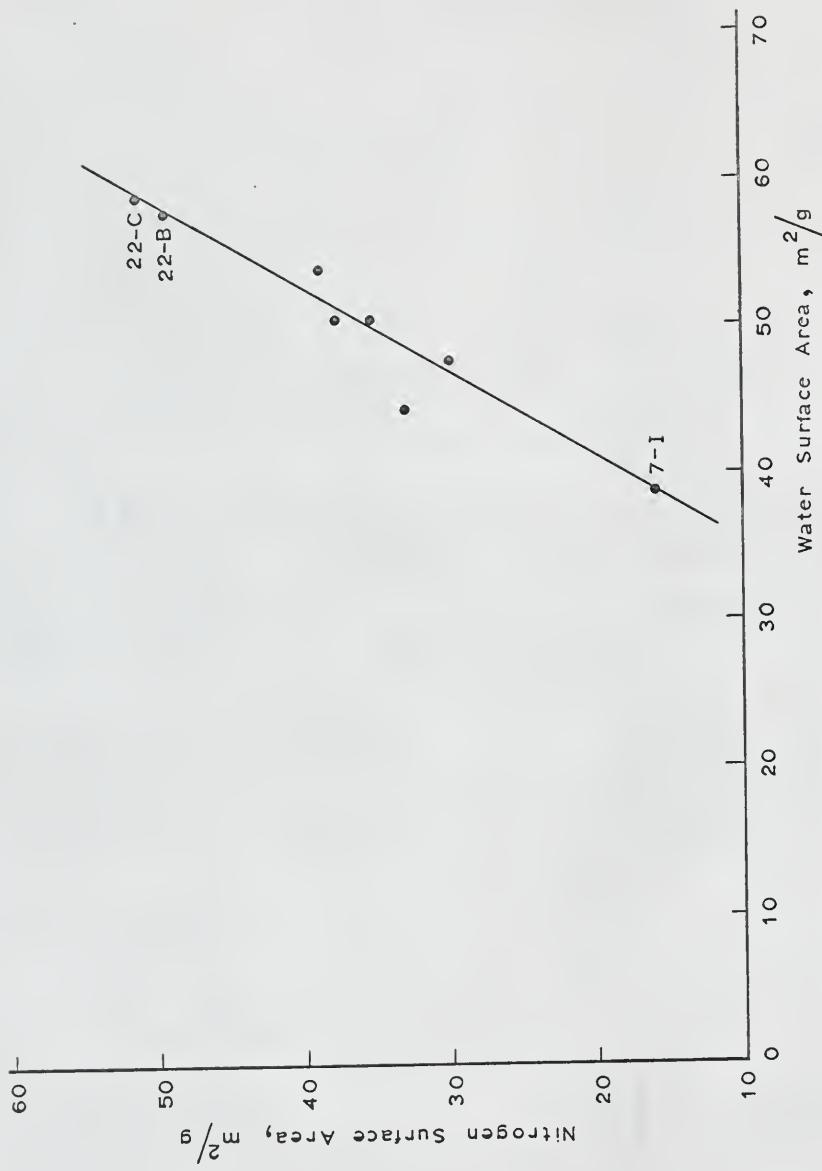


Fig. 17.-Nitrogen surface area vs. water surface area for oxalate catalysts.

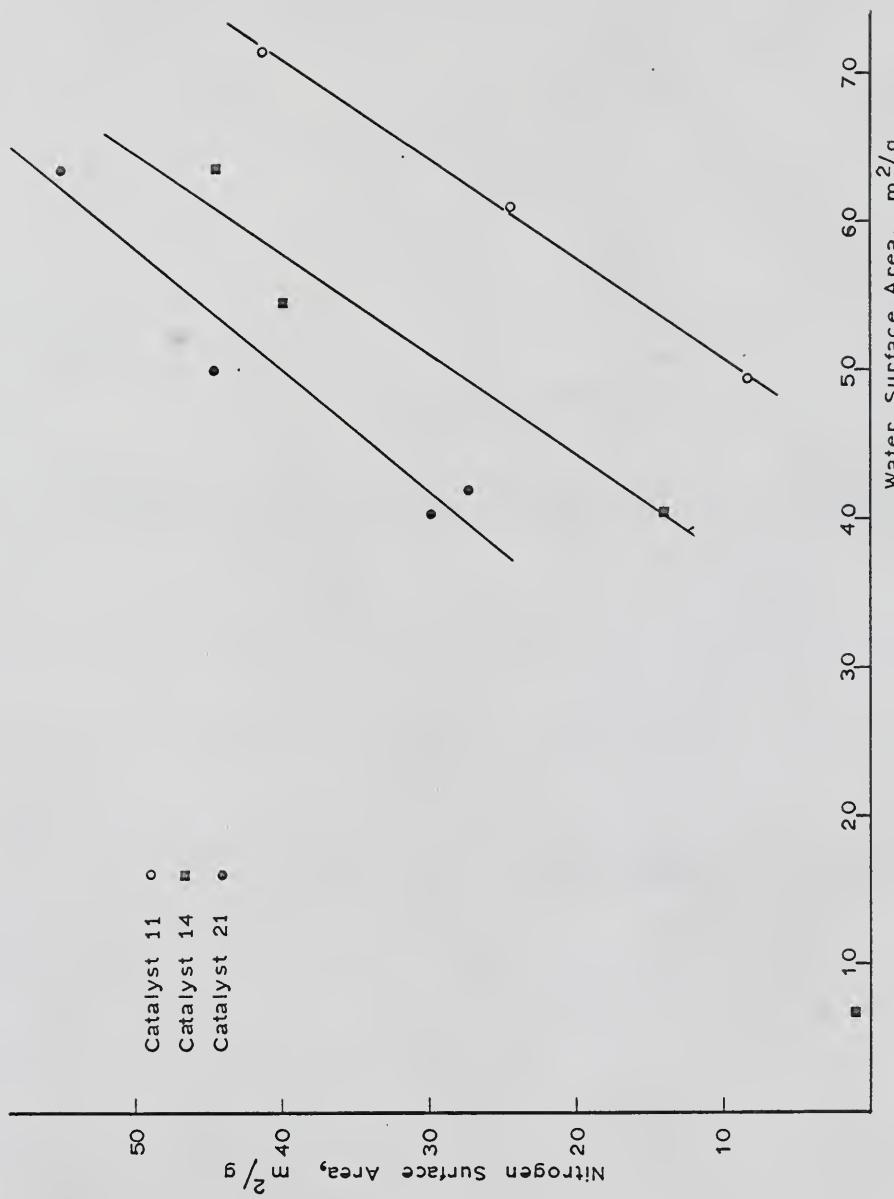


Fig. 18.-Nitrogen surface area vs. water surface area for catalyst series 11, 14, and 21. (The values plotted for catalyst series 21 were divided by two to reduce their value to the scale of the plot for the other two series.)

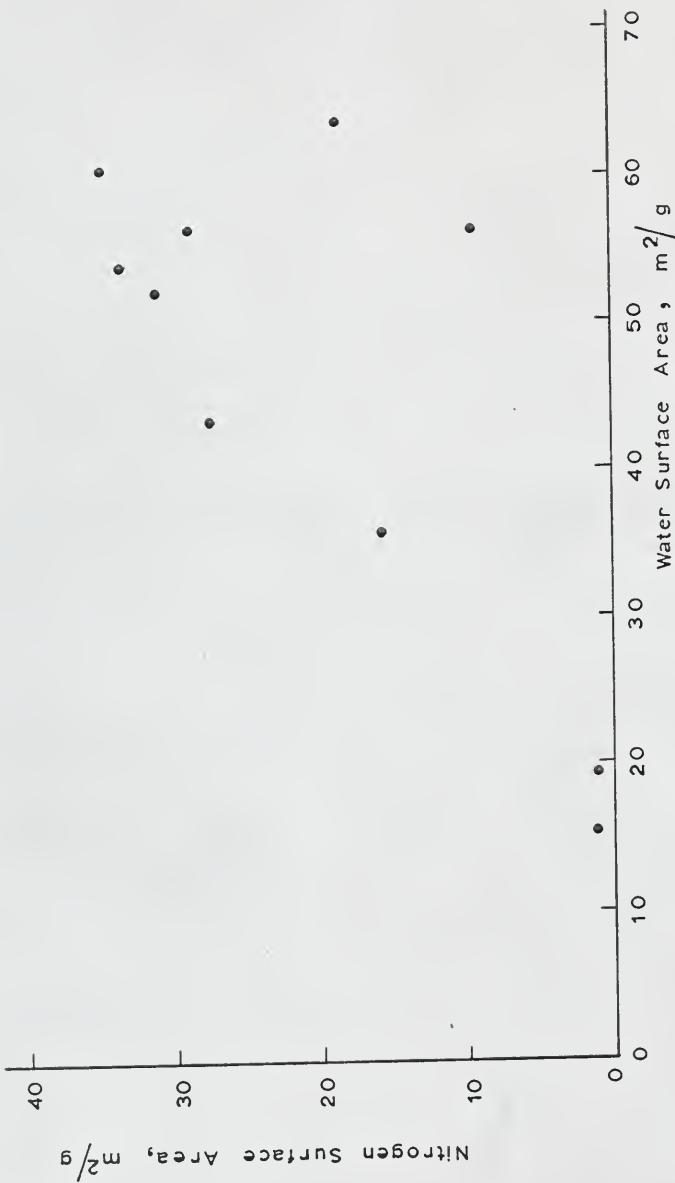


Fig. 19.-Plot of nitrogen surface area vs. water surface area for catalyst series 9.

7-I was prepared in the absence of oxides of nitrogen and the catalyst series 22 were prepared from the thorium-oxalate-hydroxide. The thoria for the points without sample designations in Figure 17 was prepared from the unwashed thorium oxalate.

This simple explanation can not be used for series 21 or 14. The slopes indicate that the nitrogen surface area increases more rapidly than the water surface area. In fact, the water surface area for the highest surface area catalyst, 21-0, is only slightly greater than the nitrogen area. The same slope can result if less of the adsorbed water is being removed by the preheating for the higher surface area materials. The fact that protons remain in or on the solid after the 400°C preheating is evident since samples 21-0 and 21-P still have sufficient protons to give rise to an observable n.m.r. signal.

The use of a larger value of σ will also cause the slope of the curve to approach unity. A value of only ca. $16 \text{ } \text{\AA}^2$ is sufficient to obtain a slope of unity for catalyst series 11 and 14; however the unreasonably large value of ca. $23 \text{ } \text{\AA}^2$ is required to reduce the slope of the 21 series to unity. The use of the larger σ also increases the magnitude of the complication discussed next.

The amount of water adsorbed in excess of that required for a monolayer of physically adsorbed water is too

large to be accounted for by chemisorption of a complete monolayer before the physically adsorbed layer. Holmes and Secoy (52) used the lattice dimensions of thorium oxide to calculate the maximum theoretical concentration of OH⁻ on the thoria surface; they found this to be 12.8 surface hydroxyls for 100 Å² of surface. Now catalyst 11-A has a nitrogen surface area of 24.4 m²/g; the theoretical hydroxyl concentration corresponds to 4.9 mg water/g for this catalyst. The water corresponding to the water surface area intercept for the plot in Figure 18 is 12.7 mg water/g which is much greater than the maximum theoretical amount that can be chemisorbed. For the catalysts presented in these figures, the only ones for which the maximum theoretical surface hydroxyl groups chemisorbed can account for the water corresponding to the intercept of the water surface area axis are 21-O and 26-K.

Another possible source of the high surface area would be for some water to be adsorbed on the walls of the sample tube. However catalyst 3-A, for which the nitrogen surface area was small, had a water surface area of only 1.6 m²/g ($\sigma = 10.6 \text{ Å}^2$). This would indicate that, if water is adsorbed on the walls of the sample tube, the amount is small compared to the water corresponding to the intercept for the catalysts considered here.

Another possible explanation would be for the sorbed water to "diffuse" into the solid structure either as water molecules or as OH⁻ groups. This would seem to be more reasonable than having this water condensed in pores with a small radius. One can estimate the pore of maximum radius in which the adsorbate will condense for a particular pressure by the Kelvin equation, $\ln(P/P_0) = 2V\gamma/RTr$ where P is the pressure, P_0 is the saturation pressure at the temperature, T, V is the molar volume, γ is the surface tension, and r is the maximum radius of a pore in which the adsorbate can condense at the pressure P. One might expect the higher surface tension of water to cause water to condense in pores with a larger radius than is possible for nitrogen; however the lower molecular volume of water and the difference in temperature for the two adsorption measurements just about offset the increase caused by the surface tension. This means that the pores in which this water is adsorbed would have to be less than ca. 10 Å radius; that is, pores in which one or two molecular layers of water will fill the pore. When one gets to dimensions of this size the concept of a pore hardly seems applicable. In fact, there would be little distinction between adsorption in a pore of this dimension and "diffusion" through the solid. This diffusion of water into the solid would explain the increase in irreversibly adsorbed water with each adsorption isotherm

measurement as observed by Draper and Milligan (46) and also in this study. If the irreversibly adsorbed water was present in pores one would not expect an increase in the irreversibly adsorbed water after the second isotherm measurement.

The nitrogen and water surface areas for series 9 catalysts are so different that they do not fall on a curve. These catalysts were prepared by precipitation from thorium solutions of different concentrations. A comparison of the ratio of water surface area to nitrogen surface area for the various thorium concentrations shows a definite trend. For the highest concentration, 1.8 M, the ratio is 2.3; from 0.9 M to 0.3 M the ratio is ca. 1.6; a further decrease in the thorium concentration produces catalysts for which the ratio increases to a high of 18.9 for the 0.03 M solution.

No really satisfactory explanation can be offered for the great differences between the surface area obtained using the two adsorbates. It appears that several types of adsorption are taking place. Measurement of heats of adsorption may shed some light on the processes involved; however, it would seem that a much better understanding of the "structure" of the thoria solid itself is necessary before one could hope to explain the water B.E.T. surface areas.

The water adsorption isotherm was measured for 21-B after preheating at 400°C. After saturation the sample was evacuated for 24 hours at room temperature and there was 15.6 mg/g of water which was not removed. A second adsorption isotherm was run after evacuation at room temperature. It is seen in Figure 20 that the second isotherm is the same as the first except it is shifted to greater amounts of adsorption for each relative pressure. The first few points for the first isotherm were obtained over a 5-7 day period and the complete isotherm was measured over a two-three week period. Thus all but exceptionally slow "re-hydration" of the surface should have occurred well before the first adsorption isotherm was completed. However, Draper and Milligan (46) observed an increase in irreversibly adsorbed water after each of four saturation and evacuation runs for several thoria catalysts derived from the oxalate and they attributed this to an aging process which required an extremely long period of time to reach completion. Peri (68) found that for alumina up to 0.53 monolayers of water was rapidly and irreversibly adsorbed. Further additions of water were incompletely adsorbed but adsorption increased slowly with time due mainly to an increase in irreversible adsorption.

The surface area calculated from the adsorptions after subtraction of the irreversibly adsorbed water was

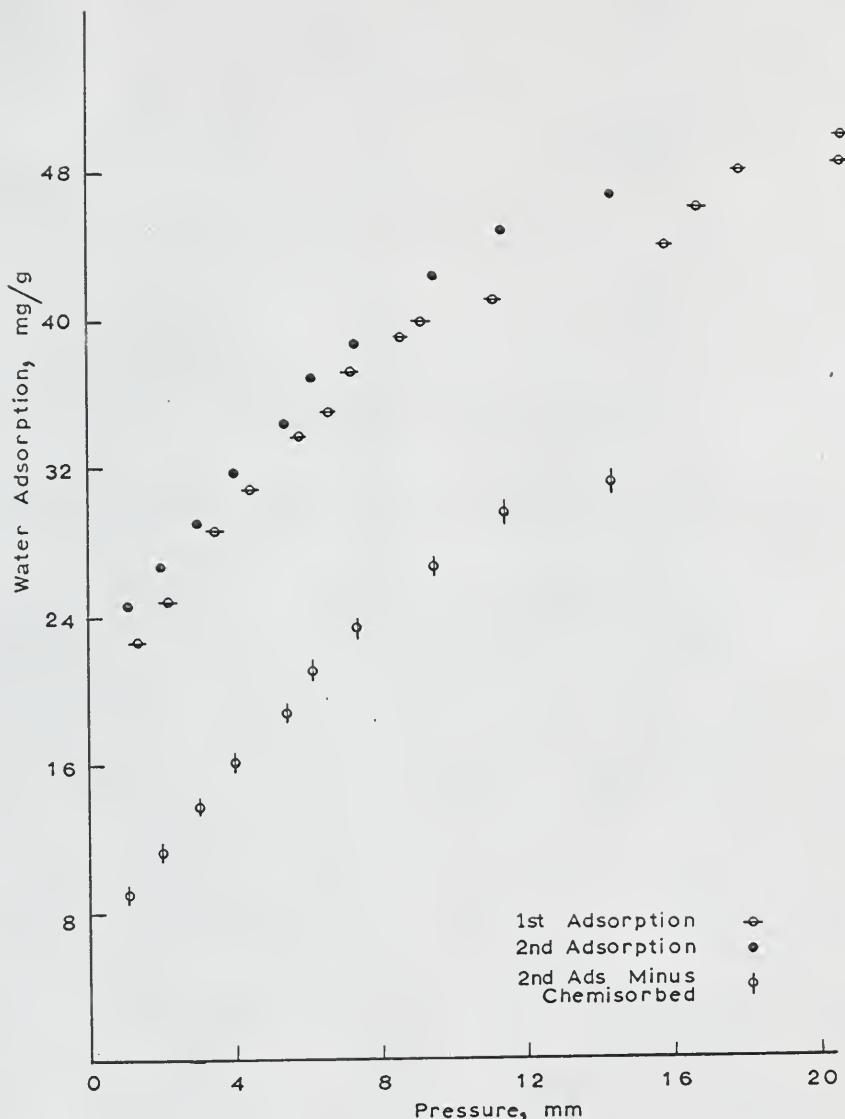


Fig. 20.-Water adsorption isotherm for catalyst 21-B.
(2nd Adsorption followed a four evacuation of sample after completing 1st adsorption isotherm.)

57.8 m^2/g which agrees closely with the nitrogen area, 59.6 m^2/g . However, the surface occupied by a water molecule, σ , was taken to be $10.6 \text{ \AA}^2/\text{molecule}$. This σ value is probably too small; indeed, Peri (68) used a σ value of $16 \text{ \AA}^2/\text{molecule}$ for water adsorption on alumina.

The water adsorption isotherms for catalysts 22-B and 22-C are quite different from the other water isotherms. A plot of the water adsorption isotherm for 22-B is shown in Figure 21 along with a plot for 7-M. The experimental points for 22-B and 22-C fit the same curve equally well except that the step at a pressure ca. 7.5 mm in the isotherm for 22-B is more pronounced than in 22-C. The larger step in the isotherm at a pressure 11-11.5 mm is very evident in both isotherms.

The stepwise isotherm has been observed before (54a, b); the best documented one is the adsorption of krypton on graphitized carbon at liquid air temperatures. Neikam (6) observed two such steps in water adsorption isotherms for alumina.

Ross and Oliver (54a) have also presented data on stepwise adsorption due to adsorption on different lattice planes; however these steps are usually observed at much lower pressures than they were for 22-B and -C.

Chapman and Halsey (69) have calculated an equation to describe the adsorption isotherm which takes into

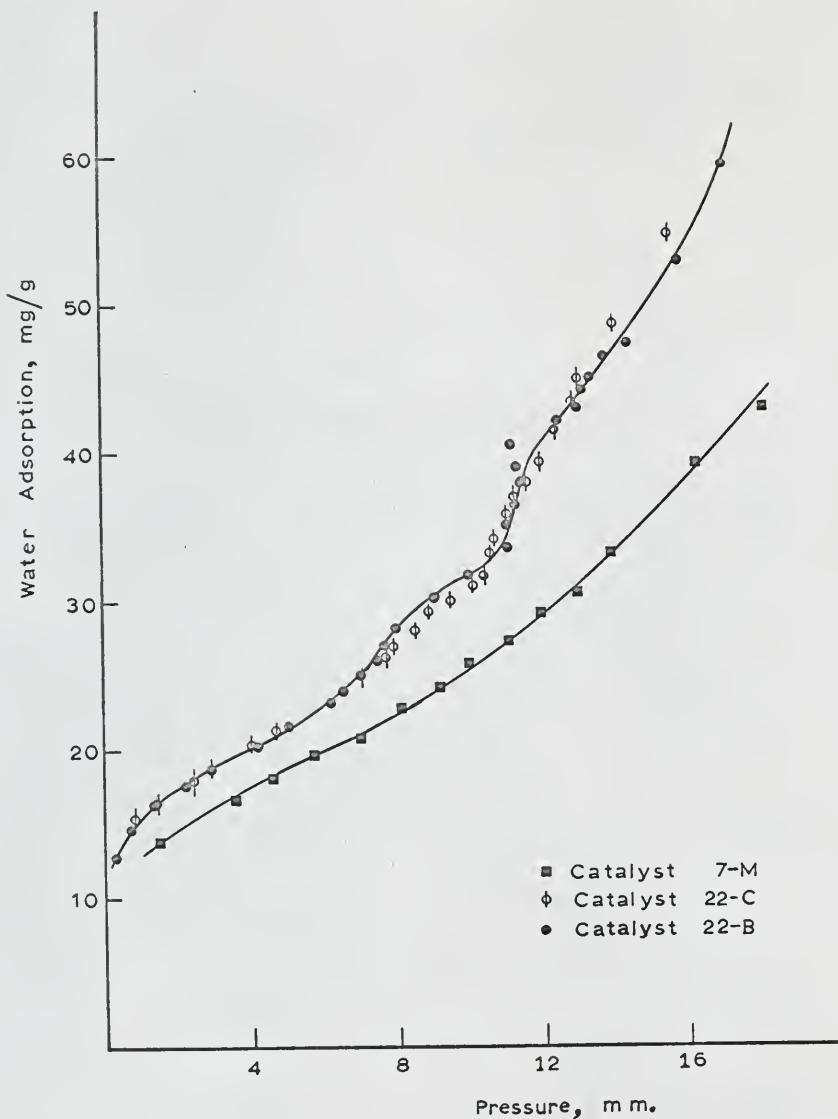


Fig. 21.-Water adsorption isotherm at 23°C for oxalate catalysts.

consideration the van der Waals forces transmitted from the surface to each succeeding layer of adsorbate and these authors concluded that multilayer adsorption on a uniform surface leads inevitably to stepwise isotherms and that smooth isotherms result because of surface heterogeneity.

If these steps are due to the completion of successive layers then these steps should occur at some multiple of the surface area, Σ . If one subtracts V_m , calculated by the B.E.T. equation using the water adsorption data, from the amount of water adsorbed at the beginning of the step at 11.2 mm a value of $\sigma_{H_2O} = 18.5 \text{ \AA}^2$ is required to make the amount of adsorbed water correspond to the nitrogen surface area; if the top of the step is taken as the amount of water adsorbed in the second layer then a value of $\sigma_{H_2O} = 14.8 \text{ \AA}^2$ is required for agreement with the nitrogen area. This latter σ_{H_2O} value is in good agreement with values used by other authors. However, this would mean that the first step, which begins at a pressure nearly corresponding to a B.E.T. monolayer, is not completed until the filling of the second layer is well underway.

Thus, while it seems that the steps are real, much more accurate isotherms must be measured and the theoretical treatment of adsorption put on firmer grounds before a decision can be made as to the reasons for these steps.

L. N.M.R. Line Width of Water Adsorbed on Thoria

Brey and Lawson (57) measured the line widths of water, butylamine, ethanol, and methanol, both as a function of surface coverage and temperature, when adsorbed on several thoria samples. All of the precipitated samples used in that study were of comparatively low surface area; the surface areas were $15.5 \text{ m}^2/\text{g}$ or less. Both oxalate samples were prepared by thermal decomposition in air of thorium oxalate obtained from Fischer Scientific Company. No analysis was given for the sample and consequently the nitrate ion content is unknown. The surface areas obtained for two preparations were 12.5 and $37.0 \text{ m}^2/\text{g}$. The preparation procedure for both samples was identical except air was circulated over the low area material during decomposition; consequently the rate of heating was slower for the low area material. The surface areas obtained by the rapid and slow heating material agree with the results of the present study provided that the commercial material contained some nitrate ions.

For one sample (surface area $9.6 \text{ m}^2/\text{g}$, activated at 600°C) there appeared to be some difference in the values obtained on adsorption and on desorption; on other samples no differences were noted. A difference in line width was noted for the adsorption and desorption measurements for all samples in this study for which desorption measurements

were made, except at very high coverages where the two line width measurements were the same. For both studies it was observed that the lines for the desorption measurements are wider than the adsorption measurements for a given coverage. Two desorption measurements were made for the samples Th-1, Th-2, Th-3, and Th-5.* Initial plans were to measure the line width for the desorption run. Thus only a few measurements of line width were made for the first adsorption. After the samples stood under the saturation water vapor pressure for about three days the desorption measurements were begun. Only a few hours were allowed to elapse between the first three desorptions, the next five desorption points were obtained the following day, and the final three desorption points were obtained the following day. A small leak in the vacuum system exposed the four samples to the atmosphere and they were reheated at 400°C under vacuum. This time the line widths for the adsorptions were measured at closer intervals of coverage. The desorption measurements were made after letting the samples stand under water vapor; however, this time at least 24 hours elapsed between the desorption and line width measurements. At least a 24 hour period was also allowed between adsorption and the line width determination. For a particular coverage for samples

* For an explanation of the designation of these n.m.r. samples and their water and nitrogen B.E.T. areas see Table 6.

Th-1, Th-2 and Th-5 the line widths for the second desorption was not as large as for the first desorption. For Th-3 little difference was observed for the two measurements. The points for the two adsorption runs agree more closely. A plot for the two adsorption and desorption measurements is presented in Figure 22 for catalyst Th-1.

Brey and Lawson (57) observed that the line width increased after standing for about two months. In the present study the line width for catalyst 22-B is also seen to increase after standing for about two months between two adsorptions. All other adsorption runs for the present studies were completed from evacuation at 400°C to saturation within one month and no evidence was observed for the line broadening for these samples. As seen in Table 10 different results are obtained for samples allowed to stand for a month or more between measurements for the desorption runs. After standing for about three months all samples showed a decrease in line width or no change in line width. After further desorptions were made standing a period of about two months again caused a decrease in line width.

These changes in line width can be interpreted as involving protons which are not very mobile. When one desorbs a small amount of adsorbed water the more mobile protons could be removed. The removal of the mobile protons would cause the line width to become broader. However,

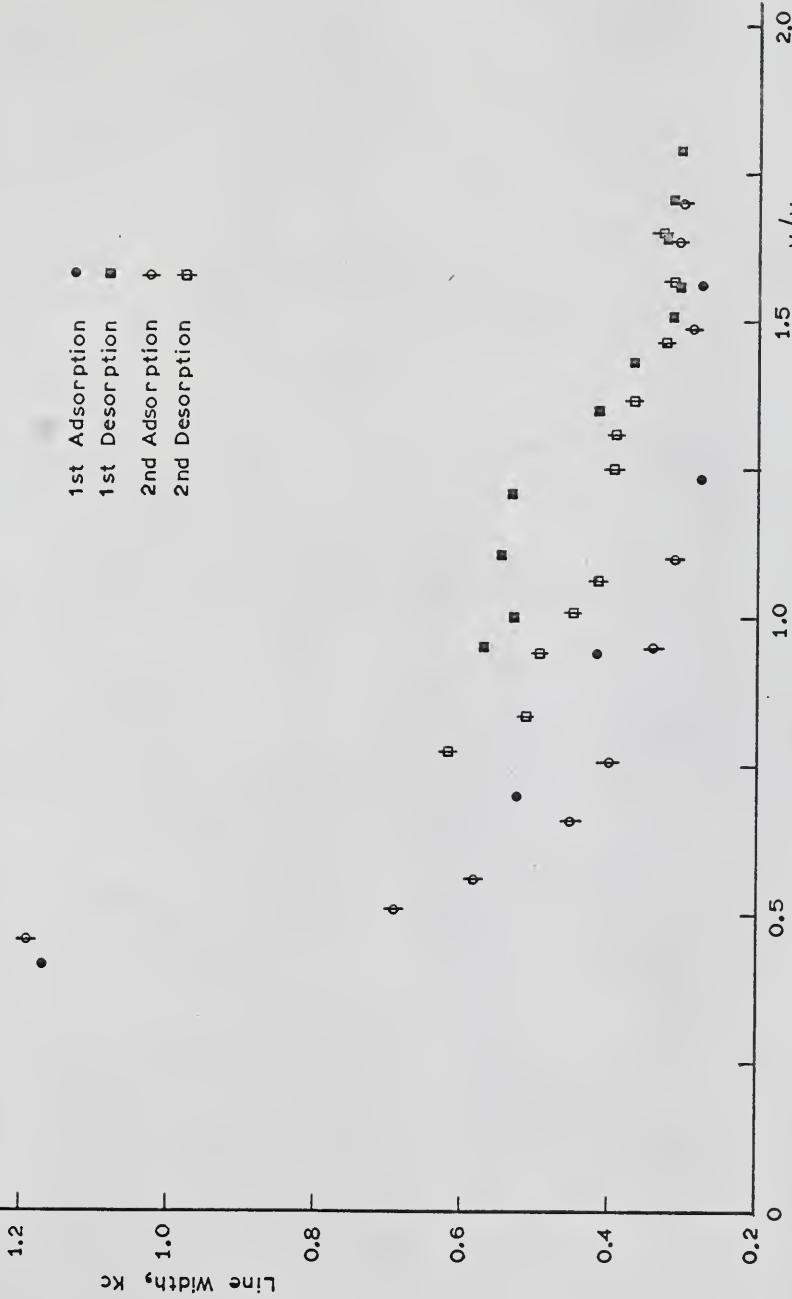


Fig. 22.-Plot of n.m.r. line width vs. surface coverage for $\text{B}_\text{E.T.}$ monolayer.

after standing for a period of time some of the rather immobile protons would become mobile to replace some of those removed in the desorption. This would then explain the decrease of the line width after desorptions. The reverse of this process would explain the broadening of the line width for the adsorptions. This explanation implies that there is an equilibrium between the more mobile and the less mobile protons and that the concentration of the less mobile protons increases with increasing total proton concentration. At least a part of the less mobile protons could be associated with the very slow hydration process described by previous authors.

Figure 23 presents a plot of the line widths versus surface coverage for some of the thoria samples. The ones presented in this figure are the extremes in line widths for a particular surface coverage and all other samples lie between these two extremes. Thus it is seen that there is not a great difference in the curves when the surface coverage is calculated from the water B.E.T. surface areas. In general the higher surface area materials produce a given line width at lower surface coverage than do the low surface area material; however there are exceptions to this generalization. One surprising result is the fact that when the surface coverage, calculated from the water B.E.T. area, is ca. 1.5 one obtains a narrow line. If the surface forces

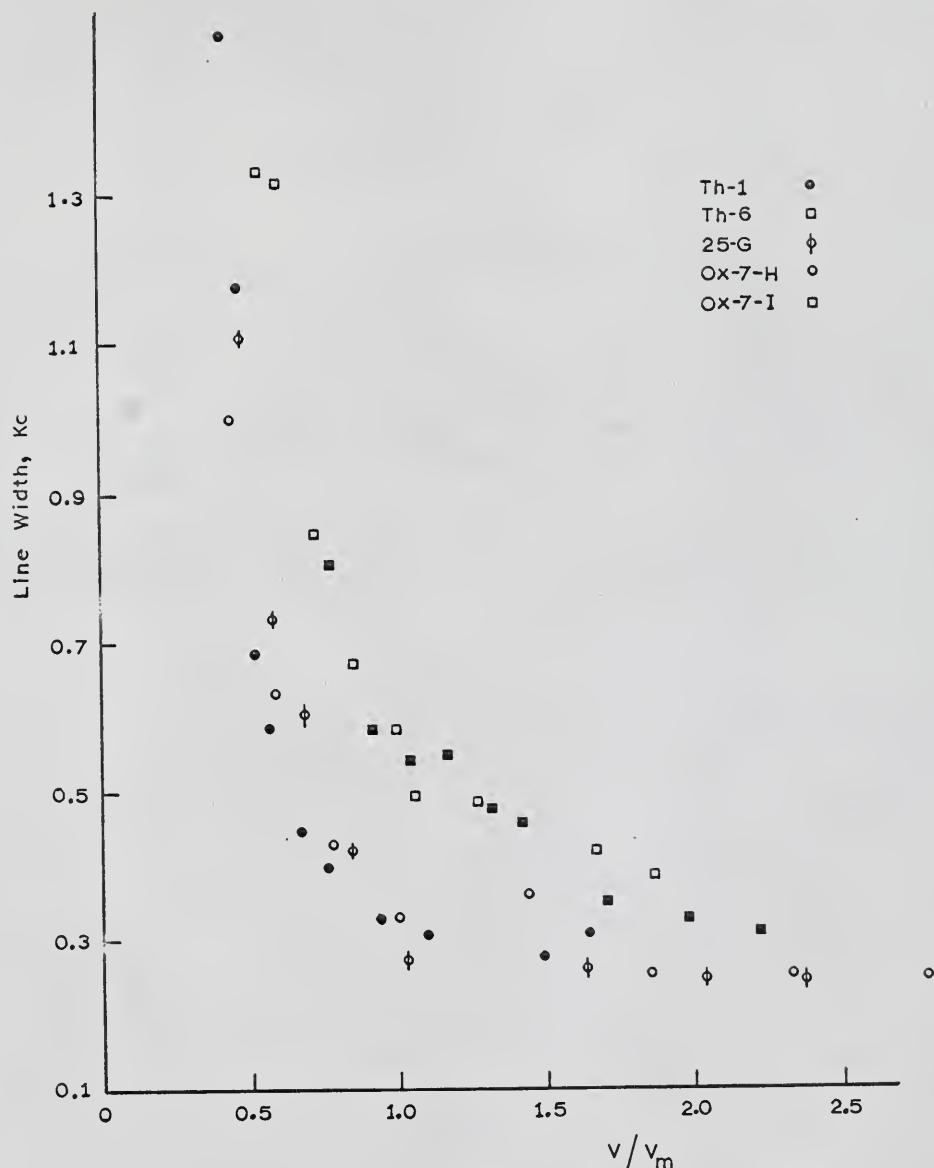


Fig. 23.-Plot of n.m.r. line width vs. surface coverage based on water B.E.T. monolayer.

extend over several monolayers one would expect the narrow line to be approached more slowly and only be obtained after a few monolayers were adsorbed.

A plot of the line width for the oxalate samples and catalyst 22-B versus surface coverage calculated using the water and the water B.E.T. areas is shown in Figures 24 and 25. It is noted that the various samples do not vary greatly; however, the lowest area material does give a wider line for a given coverage based on water surface area. A comparison of the same plot but basing the coverage on the nitrogen B.E.T. is quite similar. (The water coverage was calculated from the nitrogen B.E.T. surface area using a value of $\sigma = 14 \text{ } \text{\AA}^2/\text{volume}$ in order to compare the present results to those of Brey and Lawson (57).) The agreement between 7-H and Ox-1 is seen to be very close. The curve for catalyst 22-B is even closer to coinciding with the one for 7-H and Ox-1 than for coverage based on water B.E.T. areas. However, the curve for 7-I has been shifted to much higher coverage for a given line width. The data of Brey and Lawson (57) are also included in Figure 25. Except for low coverage the line width obtained by these authors is consistently higher than for the present study. However, the agreement is not too bad and the qualitative agreement is apparent.

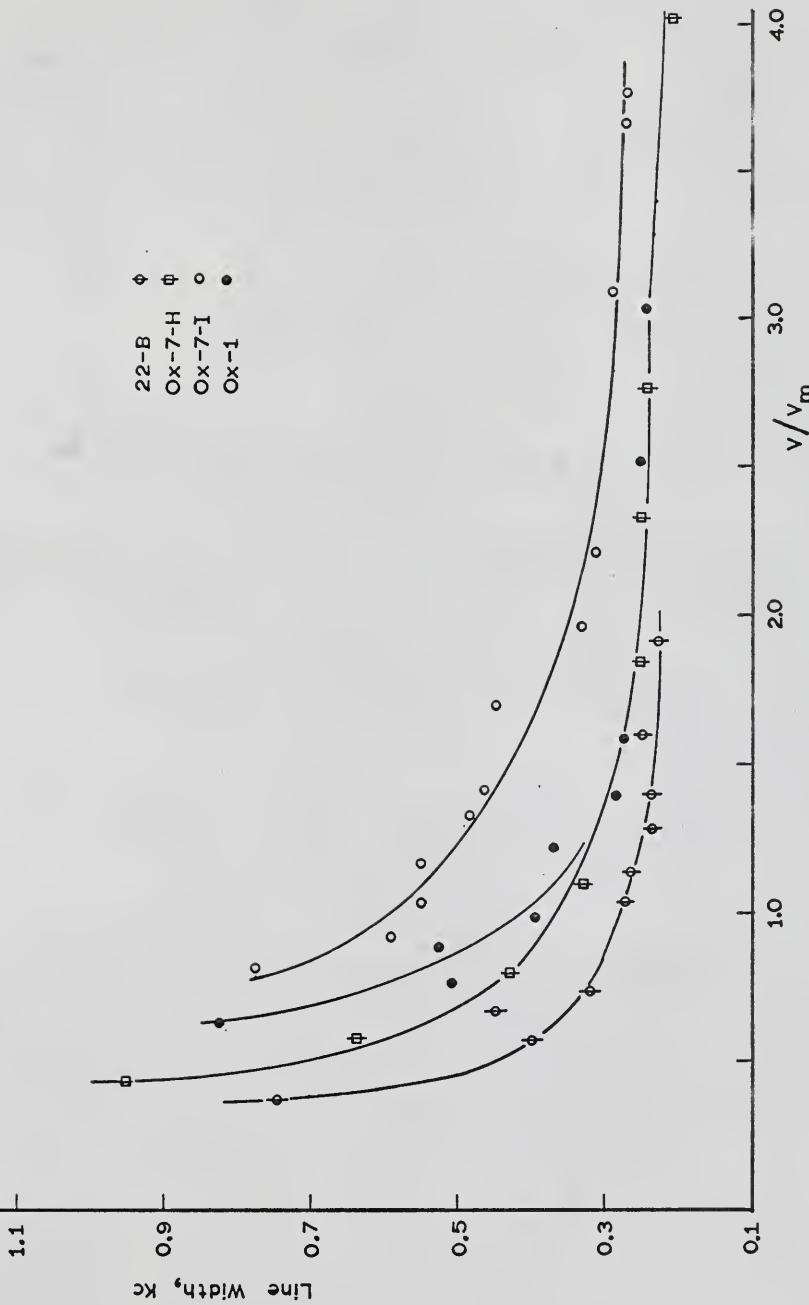


Fig. 24.-n.m.r. Line width dependence on surface coverage based on water B.E.T. monolayer for oxalate catalysts.

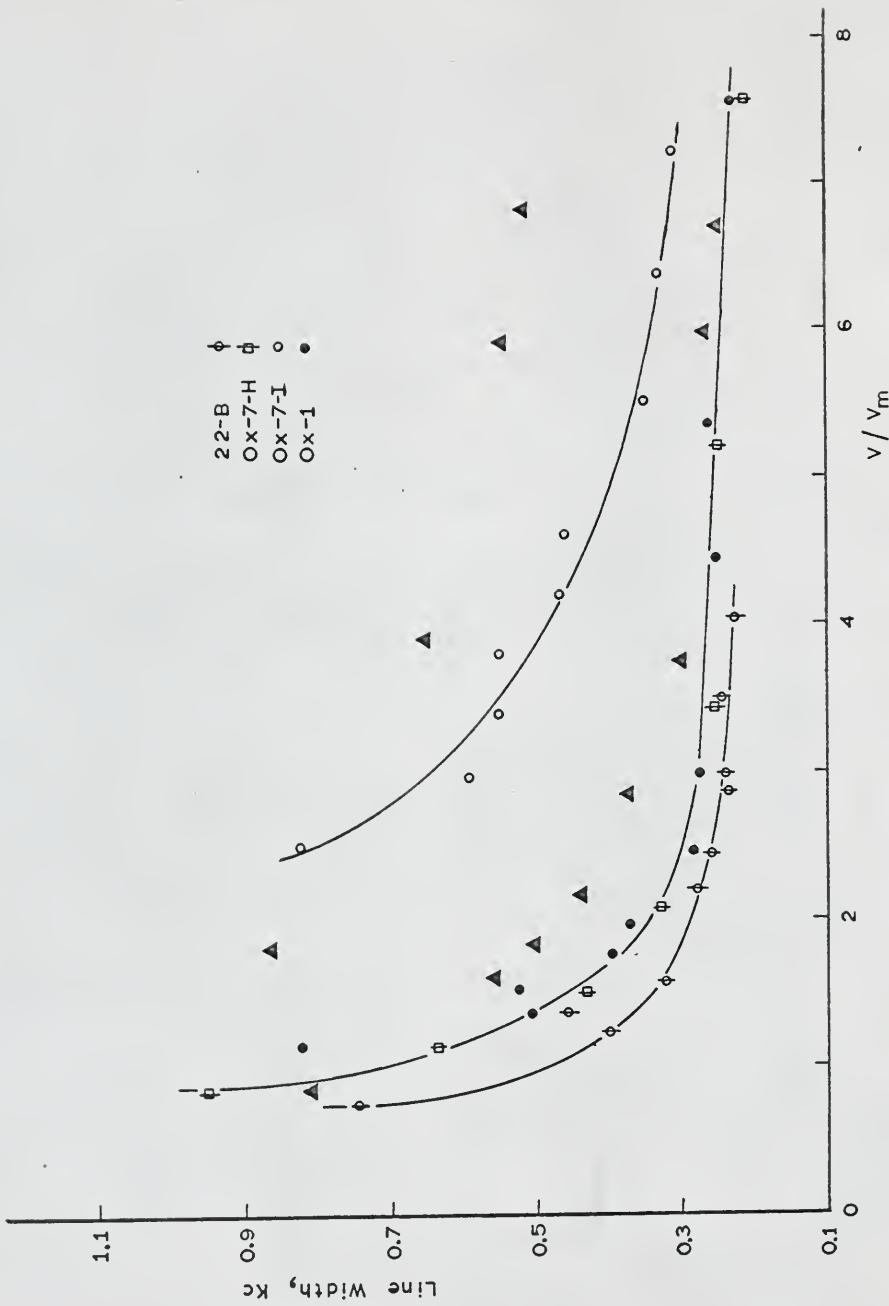


Fig. 25.—Plot of line width for oxalate catalysts vs. surface coverage based on water B.E.T. monolayer. (▲ Represents data from Reference 27.)

Evidently the relatively larger amount of water adsorbed by the smaller area catalysts is adsorbed in a less mobile state. One explanation would be that this water is adsorbed in small pores which are accessible to water but not to nitrogen molecules.

A comparison of the precipitated catalysts is presented in Figures 26 and 27 for the line width versus coverage based on water and nitrogen B.E.T. areas, respectively. The coverage based on water B.E.T. area shows little evidence of a dependence on surface area. Figure 27 shows that the curves for coverages based on the nitrogen B.E.T. areas are separated; the lower surface area samples being displaced to higher coverage for a given line width. Indeed, all five samples are displaced in the order of their nitrogen surface area. Again the relatively large amounts of water adsorbed by the smaller nitrogen B.E.T. area materials is apparently adsorbed in a less mobile state.

The line widths which have been considered in the preceding paragraphs have been the uncorrected experimental values. These lines have a contribution from the modulation field broadening and from field inhomogeneities caused by the thoria sample as was discussed by Lawson (5). Even if the observed line width were corrected for the instrumental and sample inhomogeneity broadening it is unlikely that the corrected line width would be related to a single relaxation



Fig. 26.-n.m.r. Line width vs. surface coverage based on water B.E.T. monolayer for hydroxide catalysts.

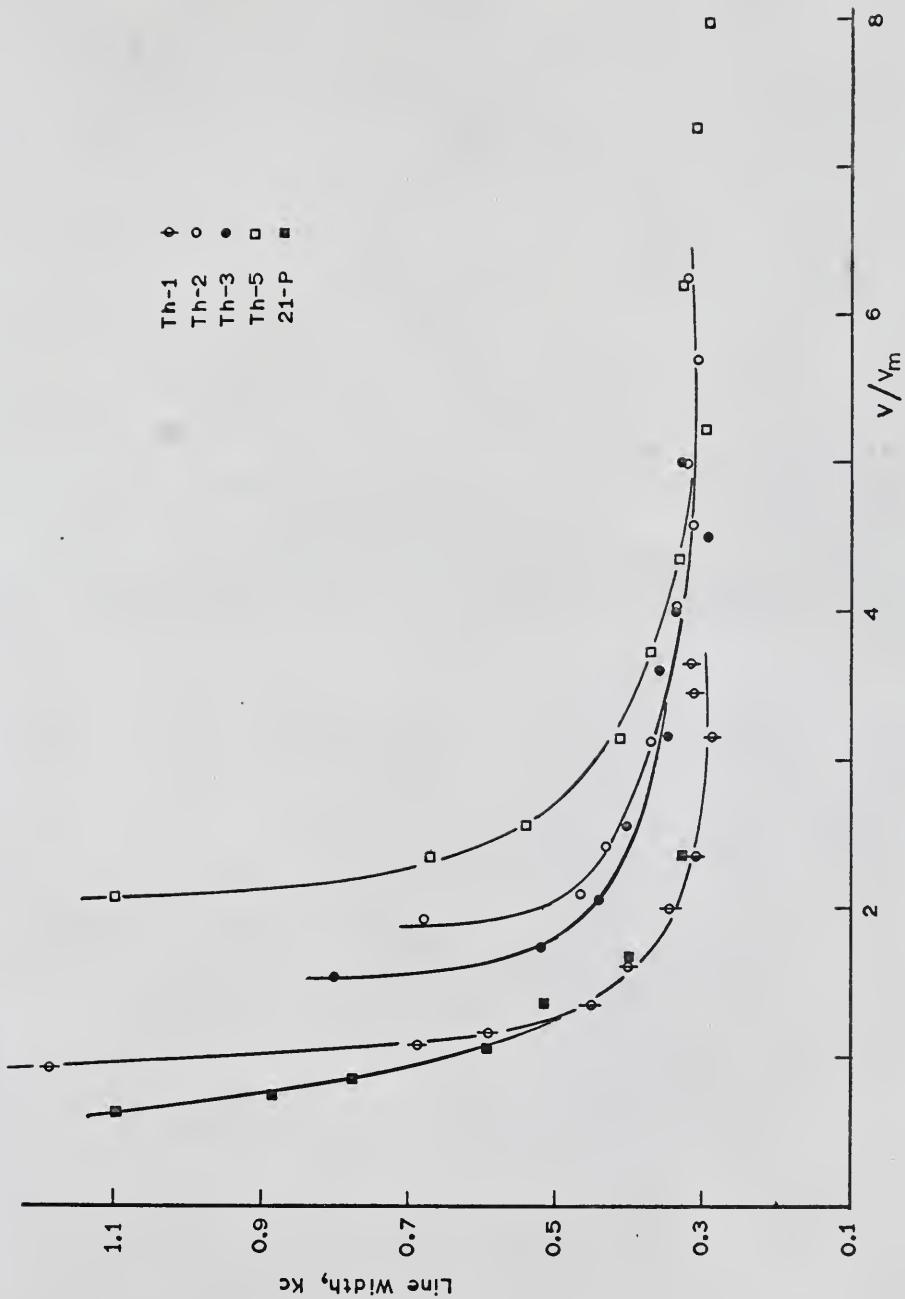


Fig. 27.-n.m.r. Line width vs. surface coverage based on nitrogen B.E.T. monolayer for hydroxide catalysts.

time T_2 . The shift, relative to each other, for the line width versus surface coverage curves when the coverage is based on the nitrogen area rather than the water area would suggest that the portion of adsorbed water which causes the relatively larger water area for the low nitrogen surface area material is being adsorbed in a relatively immobile phase to produce a wider line. As will be discussed below, there is at least one phase present which does not exchange, or at least very slowly, protons with deuterium oxide over a two-week period.

A study such as Zimmerman et al. (56) made with silica gel using a spin echo experiment could possibly distinguish between the phases if they are present. The present data indicate that such a study would be worthwhile, particularly for the samples prepared from colloidal thoria which contain enough protons after evacuation at 400°C to give a detectable signal before beginning the water adsorptions.

Catalysts 21-O and 21-P both contained protons in two distinct phases after evacuation at 400°C for four hours. A schematic representation of the spectra obtained for this catalyst after various deuterium-proton exchange processes is given in Figure 28. The amplitude of the broad peak has not been drawn to scale in order to emphasize the main changes occurring during exchanges.

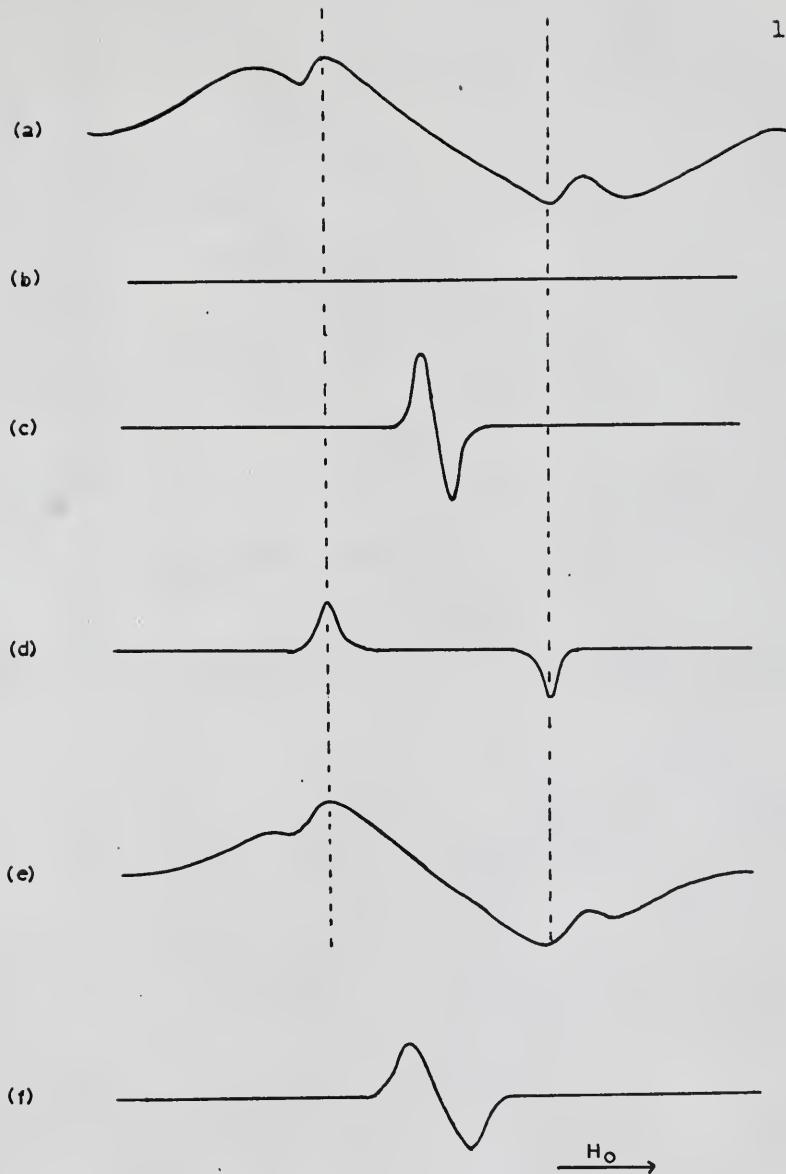


Fig. 28.-Spectrum of H_2O and D_2O adsorbed on catalyst 21-0.

- (a) After evacuation at 400°C , modulation Low $\times 5$.
- (b) After evacuation at 400°C , modulation Low $\times 1$.
- (c) After exchange with D_2O , modulation Low $\times 1$.
- (d) After exchange with D_2O , modulation Low $\times 5$.
- (e) After exchange with H_2O , modulation Low $\times 5$.
- (f) After second exchange with D_2O , modulation Low $\times 1$.

Initially the spectrum contained a very broad, small amplitude peak and the larger, narrower line width peak as shown in the reproduction in Figure 28a. The narrower of the peaks was actually much narrower than it appears to be in Figure 28a. Deuterium oxide was adsorbed on the sample after recording the above spectrum and then pumped off in about one hour. This saturation with deuterium oxide and pumping off the adsorbed material was repeated many times over a 48-hour period. After this exchange the spectrum was again recorded. No evidence of the broad peak was obtained for any modulation setting on the instrument. A strong, narrow peak was observed with the lowest modulation field setting possible on the instrument. No signal could be obtained at this modulation setting for the evacuated sample before the exchange.

Spectra were obtained for the exchanged samples at increasing modulation field settings. As the settings were increased the peak broadened and eventually only the side band peaks were observable. The position of the side bands for the higher modulation fields corresponds to those of the narrow peak in the spectrum of 21-O before D_2O exchange.

Thus the narrower peak in the spectrum (Fig. 28a) corresponds to the narrow peak in (Fig. 28c). However, this narrow peak which is present in 28a cannot be observed at the lowest modulation field as it can be for the exchanged

sample. The narrow peak can be seen for some of the intermediate settings between Low x 5 for spectra (a) in Figure 28, and the lowest setting, Low xl, for (c) in Figure 28. This indicates that when protons are on the surface the amplitude of the narrow peak is smaller than when the surface is saturated with deuterium oxide. A broadening of the narrow line by the protons on the surface would explain the reduction in amplitude while the positions of the side bands remained the same. However, this broadening could not be caused by nuclear exchange since the protons giving rise to the narrow line could not be exchanged by deuterium. Thus the line broadening must be due to the magnetic dipole coupling. Since this broadening varies at least by $1/r^3$, where r is the distance of separation of the two dipoles, many of the protons in the narrow peaks must be close to the surface. One possible model which allows the protons in the narrow peak to be unavailable for rapid exchange but still close to the surface would be for these protons to be present at isolated points along a small bundle of the long $[ThO_2]_n$ chains proposed in the discussion of the preparation of catalysts by precipitations.

The 21-O sample was allowed to stand for a week under a saturation pressure of D_2O . Then the evacuation and saturation cycle was performed several times during a 24-hour period. If the narrow peak described above was due

to isolated OH or DHO present on the surface one would expect this treatment to drastically reduce the amplitude of the narrow peak. However, this was not the case; if the amplitude was reduced it was only a slight reduction.

The sample was again evacuated and saturated with water (H_2O). The evacuation and saturation step was repeated several times during a 24-hour period. The sample was then evacuated at $400^\circ C$ under vacuum. The side-band of the narrow peak was again prominent and was of the same approximately amplitude as in (a) in Figure 28. However, the wide peak, while observable, was not as pronounced as in (a) in Figure 28.

A second exchange with deuterium oxide was performed. This time the narrow peak was present but its amplitude was smaller and the line width was greater than after the first D_2O exchange (Fig. 28, f).

M. Temperature Dependence of Line Width of Water Adsorbed on Thoria

The temperature dependence of the line width for various surface coverages was measured for Th-1, Th-3, Th-5, and Ox-1. The curves for high water coverage were nearly identical. The data at high coverage are somewhat uncertain. In most instances the temperature of the sample was decreased slowly to temperatures of 220° to $200^\circ K$ over a period of 6-10 hours. When the sample was removed from the

probe at the completion of the temperature measurements there was always an ice crystal present inside the sample tube about four cm above the top of the thoria sample. Since there was not enough water vapor in the empty space of the sample tube to account for an ice crystal of this size undoubtedly some of the sorbed water desorbed during the temperature decrease.

One would perhaps expect the opposite effect, that is, as the temperature is decreased the amount of water adsorbed should increase. However, the n.m.r. results and dielectric measurements by Lawson (5) show that the sorbed water does not freeze at 0°C. Thus if there is sufficient unadsorbed water vapor in the sample tube to form a seed ice crystal at temperatures below 0°C one would expect this ice crystal to grow as long as the water vapor pressure, in equilibrium with the sorbed material on thoria, was higher than the vapor pressure of ice at that particular temperature. At lower surface coverages, and hence lower water vapor pressure, no ice crystal was observed to form.

Catalyst Ox-1 was cooled to 228°K on July 10, 1964 and an ice crystal formed. The sample stood until July 12, 1964 and was again cooled to 220°K. The line widths obtained in the second measurements were slightly narrower than the first run, however the difference was of the order of magnitude expected for errors in calibrating the sweep

rate to give cps values. Thus it appears that ice formation does not appreciably change the nature of the water that remains sorbed on the sample.

Figure 29 presents an Arrhenius type plot for the log (line width) versus the reciprocal of the absolute temperature for the Th-5 sample. The difference between the thoria derived from the oxalate and the precipitated thoria noted by Lawson for temperatures near 30°C was not noted for Ox-1 in the present study. The existence of the line corresponding to the intermediate activation energy obtained by Lawson is not as apparent in this study. While three lines seem to fit the points for some of the coverages, other measurements appeared to consist only of a line of near zero slope for the higher temperatures and a line corresponding to the one of highest activation energy in Lawson's study for the lower temperatures.

The temperature at which the line broadening by the highest activation energy process becomes appreciable is seen to approach 0°C as the surface coverage is decreased. Indeed for a coverage of 0.36 monolayer for catalyst 22-B the higher activation process is seen to begin at room temperature (Fig. 30). One would expect, as more and more water is added, that the sorbed water would approach the liquid water state and the ice-structure would form at a temperature near 0°C.

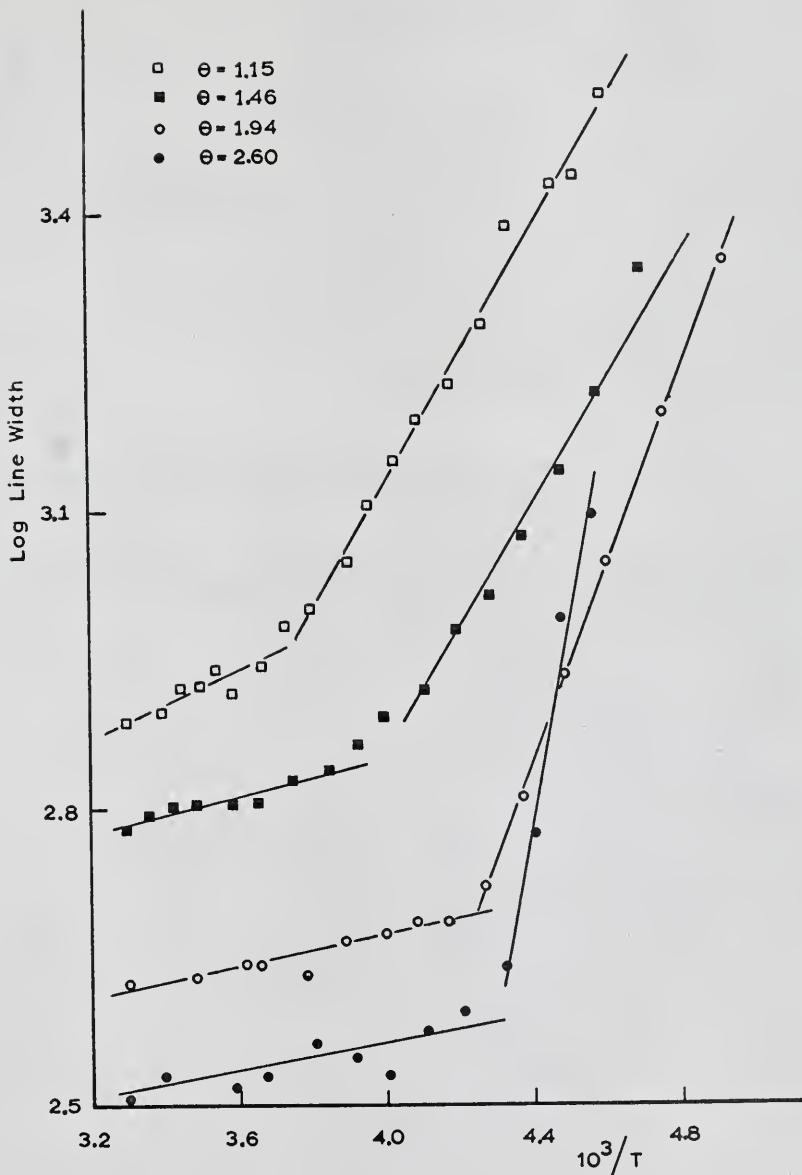


Fig. 29.-Log line width vs. reciprocal temperature for water adsorbed on Th-5. Surface coverages are based on water B.E.T. monolayer.

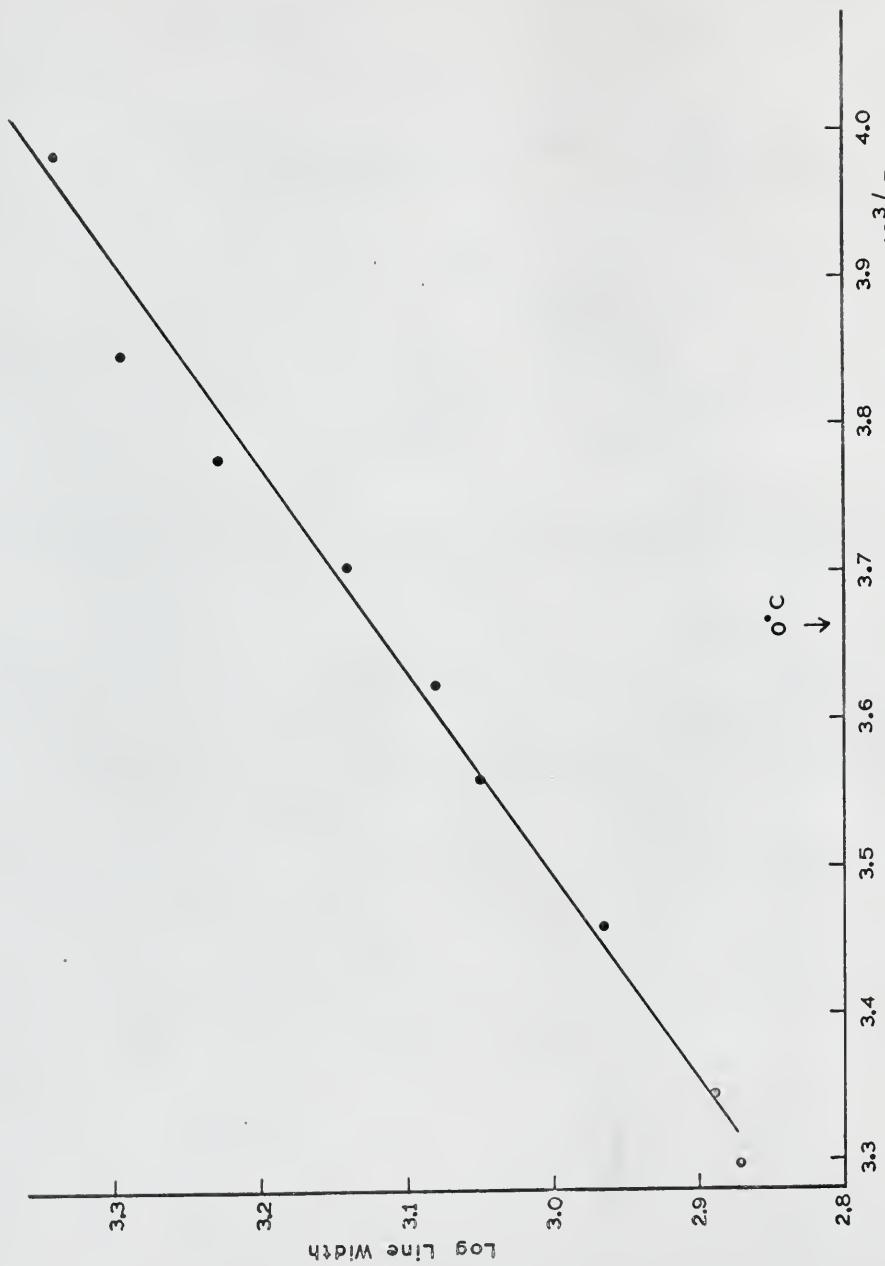


Fig. 30.—Log of the line width vs. reciprocal temperature for 0.36 monolayer of water adsorbed on catalyst 22-B.

Apparently, for the present study, a minimum temperature would be reached for this ice-like structure formation and the adsorption of more and more water would cause the freezing to again occur at temperatures that approach zero 0°C. The activation energies obtained for the lower temperatures for various surface coverage are presented in Table 9. These values agree rather well with largest activation energies obtained by Lawson (5). The activation energy increases with increasing coverage as one would expect if the water adsorbed at higher coverages is more mobile than that adsorbed at lower coverages. However, a more detailed discussion of the temperature dependence of the line width must await a more complete understanding of the nature of the adsorbed water.

CHAPTER VI

SUMMARY

The preparation of thorium oxide catalysts has been studied. Catalysts with a nitrogen B.E.T. surface area greater than $50 \text{ m}^2/\text{g}$ have been prepared by the thermal decomposition of thorium nitrate, thorium oxalate, and the precipitated hydroxide.

The effect of the variables concerned with the precipitation and subsequent treatment of the precipitate has been extensively investigated. If a large excess of base is used for the precipitation, the base must be added rapidly to obtain a large surface area thoria. The effect of washing and activating conditions depend on the history of the precipitated thoria. For the precipitation from a thorium nitrate solution the highest surface area thoria was obtained for a pH 7.0. The anion appears to influence the surface area of the thoria obtained from the precipitated material.

The rate of heating had a great influence on the surface area of the thoria obtained by the thermal decomposition of thorium nitrate and oxalate. The presence of nitrate ions enhanced the surface area of the thoria obtained by the thermal decomposition of thorium oxalate.

The highest surface area thoria was obtained from the precipitate obtained by adding base to a colloidal thoria dispersion. The surface area of the activated precipitate seemed to depend on the final pH at which the precipitation from the colloidal dispersion was performed; the optimum final pH appeared to depend on the initial pH of the colloidal thoria dispersion.

Crystallite size as determined by X-ray line broadening seemed to be determined by the activation temperature, and with the exception of the catalysts prepared from thermal decomposition of thorium nitrate, was not simply related to the surface area.

The surface areas for many of the catalysts were determined by water adsorption. The water B.E.T. surface area is not simply related to the nitrogen B.E.T. surface area. Apparently there are several types of water adsorption involved below and in the relative pressure regions for which the B.E.T. equation is valid. Adsorption isotherms were measured and appeared to be type IV according to Emmett's classification. The adsorption isotherm for a catalyst prepared from a thorium-hydroxide-oxalate mixed salt had two steps which may be due to completion of successive layers.

The wide line n.m.r. technique was used to study the adsorption of water on thorium oxide. The line width was

measured at room temperature for increasing surface coverage of water adsorbed on thoria samples prepared by different methods. No great difference was observed in the line widths at a particular coverage for the different samples when the surface coverage was based on the nitrogen B.E.T. monolayer. The variation in line width for different samples was not great, however a particular line width was obtained at a lower surface coverage for the larger surface area thoria samples. This increase in line width for a particular coverage appeared to be related to the surface area if the coverage was based on the monolayer calculated from the nitrogen B.E.T. area.

A wide and narrow line was observed for a catalyst prepared from colloidal thoria, activated at 600°C, exposed to water vapor, and then reheated to 400°C, before beginning the water adsorption. The protons causing the wide line could be exchanged with D₂O; the ones causing the narrow line could not be exchanged.

The temperature dependence of the line width for various coverages was measured. In general the activation energy, calculated from the Arrhenius equation, to "freeze" out the motion increased for increasing surface coverage and this "freezing" became noticeable at decreasing temperatures for increasing surface coverage.

APPENDIX
(Tables of Numerical Data)

TABLE 1

WATER B.E.T. SURFACE AREAS

Sample	Nitrogen Surface Area m^2/g	Water Monolayer cc/g at 25°C	Water Surface Area, m^2/g $\sigma = 10.6$	Nitrogen Surface Area After H_2O B.E.T.
3-A	0.52, 0.41	0.61	1.6	
3-E	6.75, 6.05	13.7	35.8	
9-B	28.6	21.6, 22.8	56.1, 59.6	
9-K	15.9	13.8	35.9	16.0
9-M	27.4	16.6	43.2	26.3
9-N	31.2	20.0	52.0	29.8
9-O	33.5	20.7	53.8	30.7
9-E	1.1	7.3	19.1	
9-C	18.6	24.3	63.5	
9-A	34.8	23.0	60.1	
9-G	1.1	6.1	15.5	
9-D	9.3	21.4	56.1	
7-E	29.9	18.3	47.7	
7-H	35.2	19.3	50.4	
7-I	15.8	14.9	38.8	
7-J	33.0	16.9	44.2	
7-N	37.8	19.3	50.3	
7-M	38.9	20.6	53.9	
11-A	24.4	23.6	61.5	
11-B	8.3	19.0	49.5	
11-E	41.2	27.4	71.5	
12-A	37.8	23.3	60.8	34.6
12-C	53.5	26.3*	67.7*	
		30.2**	78.8**	43.5**
12-D	18.9	16.1	42.0	16.7
12-E	0.9	3.5	9.2	
14-B	1.0	2.6	6.9	
14-C	28.9	15.6	40.6	13.1, 16.1
14-E	44.4	22.6*	58.8	
		24.5**	63.7	34.8
14-F	42.1	20.9	54.5	40.3, 40.3
17-A	57.2	31.2*	81.5*	
		32.4**	84.5**	50.2, 50.0
18-E	46.9	27.5	71.6	
21-B	59.6	30.9	80.5	
21-O	110	48.7	127	94

TABLE 1 - Continued

Sample	Nitrogen Surface Area m^2/g	Water Monolayer cc/g at 25°C	Water Surface Area, m^2/g $\sigma = 10.6$	Nitrogen Surface Area After H_2O B.E.T.
22-B	49.3	22.2	57.8	
22-C	51.3	22.5	58.8	
22-G	10.6	6.1	15.9	
25-G	55.5	25.4	66.4	
25-D	29.0	17.4	45.5	
26-K	89.4	37.6	98.5	

*After evacuation at 250°C for four hours.

**After evacuation at 400°C for four hours after the 250°C evacuation.

TABLE 2

AVERAGE CRYSTALLITE SIZE AS DETERMINED BY X-RAY LINE BROADENING

Catalyst	Average Size, Å	Catalyst	Average Size, Å
2-A	100	4-A	91.6
2-B	109	4-B	91.6
2-F	76.9	4-C	92.9
2-G	93.8	4-D	101
2-I	100	4-E	89.0
2-J	89.0	4-F	94.4
2-K	93.8	4-G	92.9
2-L	90.6	4-H	88.0
2-M	81.7	4-I	98.5
2-O	83.9	4-J	83.2
2-P	79.5	4-K	89.9
		4-L	92.9
3-A	120	4-M*	102
3-B	89.0	4-N*	101
3-C	96.4	4-O*	100
3-D	94.4	*After several reactivations	
3-E	93.8	5-A	92.9
3-H	115	5-B	85.5
3-I	81.0	5-C	96.4
3-F	85.5	5-D	92.9
7-A	70.9	5-E	89.0
7-B	68.7	5-F	83.2
7-C	116	5-G	81.7
7-E	116	5-H	87.2
7-H	115	5-I	91.6
7-I	138	5-J	78.9
7-G	181	5-K	85.5
7-K	150	12-A	91.6
7-O	116	12-B	53.5
8-A	87.2	12-C	78.2
8-B	80.2	12-D	116
8-C	83.9	12-E	198
8-D	88.0	12-F	111
8-E	88.0	12-G	57.2
8-F	82.4	12-H	70.9
8-G	85.5	12-I	213
8-H	87.2	12-J	123
		12-K	66.8
9-A	91.6	12-L	90.6
9-B	87.2	12-M	207
9-C	87.2	12-N	576
9-D	89.9	12-O	324
9-E	83.9	12-P	97.4
9-F	88.0	12-Q	89.0

TABLE 2 - Continued

Catalyst	Average Size, A	Catalyst	Average Size, A
9-G	83.9	21-A	101
9-H	112	21-B	75.6
9-H*	107	21-C	93.8
9-I	81.0	21-D	90.6
9-I*	82.4	21-F	85.5
9-J	89.9	21-G	78.2
9-J*	92.9	21-H	66.8
9-K	98.5	21-J	92.9
9-L	108	21-K	94.4
9-M	96.4	21-L	71.4
9-N	96.4	21-M	70.9
9-O	89.0	21-N	70.9
9-P	113	21-O	62.6
9-F*	90.6	21-P	61.4
*Duplicate Measurements		21-E	94.4
10-A	85.5	22-A	89.0
10-B	79.5	22-B	103
10-C	83.9	22-C	96.4
10-D	83.9	22-D	92.9
		22-F	230
11-A	88.0	22-G	352
11-B	86.3	22-H	245
11-C	75.6	22-I	140
11-D	76.2		
11-E	80.2	24-A	140
11-F	83.2	24-B	72.5
11-G	74.3	24-C	112
11-H	83.9	24-D	97.4
		24-E	82.4
13-A	87.2	24-G	93.8
13-B	84.7		
13-C	87.2	26-A	70.9
13-D	79.5	26-B	63.9
13-E	84.7	26-D	54.7
13-F	85.5	26-E	76.2
		26-G	80.2
25-A	134	26-I	79.5
25-B	320		
25-C	198	27-B	61.8
25-D	142	27-C	64.3
25-E	374		
25-F	224	30-E	80.2
25-G	91.6	30-H	74.3
25-H	193	30-B	85.5

TABLE 2 - Continued

Catalyst	Average Size, A	Catalyst	Average, Size, A
23-B	115		
23-C	72.5		
23-D	72.5		
23-E	78.2		

TABLE 3

LOSS OF SURFACE AREA BY PROLONGED HEATING

Heating Time Hours	Surface Area, m ² /g	Heating Time Hours	Surface Area, m ² /g
<u>Catalyst 4-M</u>		<u>Catalyst 4-N</u>	
4	27.9	4	36.8
21	20.9	16	23.8
33	16.9	28	16.1
43	13.3	37	19.9
53	9.4	49	17.4
64	10.3		
<u>Catalyst 17-A</u>		<u>Catalyst 4-O</u>	
4	57.2	4	35.0
11	44.9	16	22.8
22	44.0	28	18.6
48	34.6	40	16.3
62	33.8	50	14.9
77	28.5		
<u>Catalyst 18-C</u>		<u>Catalyst 18-D</u>	
4	33.0	4	47.3
10	28.2	11	33.9
22	22.7	19	28.2
<u>Catalyst 18-I</u>		<u>Catalyst 18-G</u>	
4	39.2	4	41.6
10	32.6	11	37.0
20	27.6	24	30.0
<u>Catalyst 23-F</u>		<u>Catalyst 25-I</u>	
4	38.4	4	38.4
14	74.1	14	39.5
24	70.6, 71.9	24	39.2
60	64.5	60	38.4
96	57.6	96	36.5

TABLE 4

ADSORPTION OF NITROGEN BY THORIUM OXIDE

Pressure, cm	Adsorption		Desorption	
	Volume, cc/g		Pressure, cm	Volume, cc/g
<u>Catalyst 12-B</u>				
19.50	17.855	-----	-----	-----
35.40	20.146	25.20	20.362	
61.92	21.713	61.73	21.826	
78.06	29.192	77.96	29.230	
13.35	16.582	-----	-----	-----
23.50	18.943	23.50	18.942	
39.22	21.097	38.45	21.552	
59.45	22.104	59.11	22.231	
10.25	15.878	-----	-----	-----
17.85	17.900	-----	-----	-----
29.00	20.002	28.95	20.032	
42.36	21.343	41.21	21.771	
62.35	22.224	61.52	22.422	
9.54	15.518	-----	-----	-----
16.53	17.488	16.58	17.435	
26.75	19.499	26.70	19.528	
38.59	21.049	37.29	21.400	
55.90	21.933	55.75	21.969	
14.34	16.841	14.37	16.778	
25.45	19.155	25.45	19.153	
42.97	21.193	42.48	21.518	
65.78	22.055	65.31	22.231	
18.60	17.912	18.52	18.077	
33.30	20.169	33.40	20.492	
58.40	21.983	58.20	22.101	
77.51	27.591	77.26	27.681	
14.92	17.048	14.92	17.048	
26.60	19.324	26.58	19.347	
45.05	21.375	44.62	21.629	
69.09	22.233	68.71	22.375	

TABLE 5

WATER ADSORPTION ISOTHERMS

Pressure, mm	Water Adsorbed mg/g	Pressure, mm	Water Adsorbed mg/g
<u>Catalyst 4-L</u>		<u>Catalyst 22-B</u>	
1.2	11.9	0.3	12.9
2.0	13.2	0.7	14.7
3.0	14.7	1.3	16.4
4.0	16.5	2.2	17.7
5.1	18.6	2.9	18.8
6.2	20.2	4.2	20.2
7.8	22.7	5.0	21.7
9.0	25.2	6.2	23.2
11.8	27.6	6.5	24.0
14.1	29.2	7.0	25.0
15.2	31.4	7.5	26.2
19.1	34.7	7.7	27.0
18.0	36.4	8.0	28.2
		9.1	30.8
<u>Catalyst 22-G</u>		10.0	31.8
2.6	4.8	11.1	33.6
4.0	4.8	11.3	35.0
4.5	5.4	11.6	36.4
6.4	6.0	11.4	38.0
7.4	7.0	11.2	38.9
8.7	7.9	12.5	40.4
10.4	8.3	13.0	42.1
10.9	8.6	13.1	43.0
Evacuate two hours	3.4	13.4	44.3
5.8*	6.4	13.7	45.1
8.8*	7.1	14.4	46.5
10.7*	8.0	13.5	47.3
11.7*	8.9	14.3	48.3
13.5*	9.9	15.8	50.8
14.9*	11.7	15.8	53.0
18.2*	19.7	17.1	57.7
			59.6
*Second Adsorption Run			
<u>Catalyst 22-C</u>		<u>Catalyst 21-B</u>	
0.8	15.3	1.2	22.6
1.4	16.5	2.1	24.8
2.4	18.0	3.4	28.6
2.9	19.0	4.4	30.9
4.0	20.5	5.7	33.8
4.7	21.4	6.5	35.1
5.6	23.0	7.2	37.3

TABLE 5 - Continued

Pressure, mm	Water Adsorbed mg/g	Pressure, mm	Water Adsorbed mg/g
7.1	24.8	8.5	39.1
7.7	26.1	9.1	39.9
7.9	26.8	11.1	41.3
8.5	27.8	15.8	44.0
9.0	29.1	16.5	46.0
9.5	29.9	17.8	48.2
10.2	31.0	Saturated at 20.7	50.1
10.5	31.7	Evacuate 14 hours	15.6
10.7	33.2	1.1*	24.7
10.8	34.3	2.0*	26.9
11.0	35.8	3.0*	29.3
11.3	36.9	4.0*	31.8
11.6	38.0	5.3*	34.6
12.1	39.2	6.1*	36.7
12.4	40.1	7.3*	38.8
12.3	41.7	9.4*	42.5
12.8	43.4	11.4*	45.3
13.0	45.1	14.5*	46.8
13.4	45.0	<u>Catalyst 21-0</u>	
13.9	48.8		
15.5	55.5		
17.3	60.5	1.1	31.4
<u>Catalyst Ox-4</u>		2.2	36.2
1.5	13.8	3.0	40.5
3.6	16.7	4.1	43.4
4.6	18.1	5.5	50.1
5.7	19.6	7.4	55.3
7.0	20.8	8.5	58.5
8.1	22.8	8.9	62.6
9.2	24.2	11.0	66.2
10.0	25.7	11.4	69.0
11.1	27.3	12.1	71.3
12.0	29.1	12.3	74.1
13.0	30.5	12.7	78.7
16.2	39.0		
18.1	42.8		

TABLE 6
SUMMARY OF N.M.R. SAMPLES

N.M.R. Samples	Catalyst Preparation	Nitrogen Surface Area, m ² /g	Water Surface Area, m ² /g
Th-1	17-A	57.2	84.5
Th-2	9-M	27.4	43.2
Th-3	9-O	33.5	53.8
Th-5	9-K	15.9	35.9
Th-6	19-A	39.3	(not determined)
Ox-1	7-M	33.0	44.2
Ox-7-H	7-H	35.2	50.4
Ox-7-I	7-I	15.8	38.8
21-P	21-P	114	(not determined)
25-G	25-G	55.5	66.4
22-B	22-B	49.3	57.8

TABLE 7

DEPENDENCE OF LINE WIDTH ON SURFACE COVERAGE

Water Adsorbed mg/g	Line Width cps	Water Adsorbed mg/g	Line Width cps
<u>Catalyst Th-1</u>		<u>Catalyst Th-1</u>	
First Adsorption		Second Adsorption	
9.9	1,170	8.7	1,290
16.9	525	9.8	1,530
22.4	414	10.1	1,190
29.4	274	12.1	690
35.8	275	13.3	586
		15.7	450
First Desorption		18.0	400
		22.6	341
42.4	306	26.2	310
40.6	314	35.3	288
39.0	324	38.7	313
37.3	308	40.4	328
36.0	317	Second Desorption	
34.2	371	39.3	328
32.1	419	37.3	313
28.8	535	35.0	326
26.5	546	32.6	366
24.0	529	31.1	396
22.6	571	29.8	394
		26.8	417
		24.6	446
		22.4	497
		19.8	511.
		19.5	543
		18.4	620
<u>Catalyst Th-2</u>		<u>Catalyst Th-3</u>	
First Adsorption		First Adsorption	
17.4	486	9.7	1,140
22.8	444	17.0	502
24.6	358	23.5	440
29.0	384	28.7	327
		32.0	298
First Desorption		First Desorption	
43.3	294	38.2	311
40.8	430	36.7	354
39.1	390		

TABLE 7 - Continued

Water Adsorbed mg/g	Line Width cps	Water Adsorbed mg/g	Line Width cps
37.5	453	35.0	351
35.6	478	33.4	362
33.9	484	31.8	356
31.4	458	30.4	365
29.0	554	27.7	430
26.7	574	25.2	540
24.7	645	23.0	580
23.2	685	21.0	591
		29.7	628
Second Adsorption		Second Adsorption	
11.3	680	10.0	1,380
12.3	465	11.0	800
14.3	432	12.5	518
18.5	367	14.8	440
23.6	337	18.4	406
26.2	310	22.6	344
29.2	319	25.4	360
33.4	308	28.6	338
39.6	320	32.4	291
		35.8	328
Second Desorption		Second Desorption	
38.2	368	34.1	351
36.5	353	32.1	339
32.0	385	30.8	395
28.0	426	28.9	383
25.0	426	27.4	422
22.2	552	26.6	468
20.3	635	25.0	508
18.1	707	22.8	556
		19.5	582
<u>Catalyst Th-5</u>		<u>Catalyst Th-6</u>	
First Adsorption		Adsorption	
15.0	417	9.7	1,350
20.4	430	10.7	1,330
25.7	436	11.7	857
29.1	399	14.7	675
		16.9	580

TABLE 7 - Continued

Water Adsorbed mg/g	Line Width cps	Water Adsorbed mg/g	Line Width cps
First Desorption			
33.0	320	29.4	498
31.2	390	32.7	493
29.6	472	36.7	420
28.6	481		392
26.6	580		342
25.0	515		
22.6	521	<u>Catalyst Ox-1</u>	
20.8	566	First Adsorption	
19.3	628	7.9	822
17.5	645	9.5	507
16.6	727	10.9	527
		12.3	394
Second Adsorption		13.8	370
		17.3	283
6.1	1,050	20.8	276
7.1	1,100	31.2	248
7.9	667	37.8	262
8.7	540	53.4	228
9.5	630	60.5	200
10.7	413	62.8	195
12.6	368		
14.8	333	First Desorption	
17.7	299		
21.1	332	52.9	224
24.7	313	50.2	259
27.1	296	47.5	241
29.0	283	45.0	249
		43.2	252
Second Desorption		35.2	239
		28.9	258
27.9	302	24.3	266
26.2	310	20.2	376
24.2	402	14.0	537
22.5	375		
21.0	441	<u>Catalyst Ox-7-H</u>	
19.6	461	Adsorption	
16.8	538		
14.8	586		
13.2	625	6.3	953
11.6	780	8.4	636
		11.2	426
		15.7	322

TABLE 7 - Continued

Water Adsorbed mg/g	Line Width cps	Water Adsorbed mg/g	Line Width cps
<u>Catalyst Ox-7-I</u>			
8.5	822	26.2	246
10.1	589	33.1	253
11.5	546	39.2	245
12.9	551	57.0	213
14.6	483	63.9	208
15.6	462		
18.8	346		<u>Catalyst 22-B</u>
21.6	329		Adsorption
24.4	311	5.2	1,845
34.1	296	7.9	745
40.3	276	12.7	398
41.0	276	14.4	454
48.4	265	16.6	320
		23.1	274
<u>Catalyst 21-P</u>			
		25.5	262
		28.7	236
Adsorption		31.3	238
		36.5	245
2.6	9,400	42.4	227
4.1	8,700		
9.7	7,200		<u>Catalyst 25-G</u>
12.1	1,600		
15.2	1,100		Adsorption
18.3	885		
20.9	777	3.7	640
26.0	593	6.3	999
32.9	518	8.5	1,120
40.7	401	10.5	750
56.6	322	13.0	600
		15.9	430
		19.0	280
		30.4	270
		38.1	246
		43.8	256

TABLE 8

TEMPERATURE DEPENDENCE OF LINE WIDTH

Temperature, °C	Line Width, cps	Temperature, °C	Line Width, cps
<u>Catalyst Th-1</u>		<u>Catalyst Th-3</u>	
37.3 mg H ₂ O/g ThO ₂		32.1 mg H ₂ O/g ThO ₂	
30	305	30	339
15	348	22	334
-5	370	11	347
-12	376	1	328
-19	376	-10	326
-27	402	-17	356
-36	467	-24	370
-41	512	-29	373
-46	613	-34	392
-50	775	-39	446
-56	1,050	-46	725
29.8 mg H ₂ O/g ThO ₂		-52	1,030
		-58	1,530
30		26.6 mg H ₂ O/g ThO ₂	
8	368	30	435
-3	414	8	445
-8	424	-8	437
-14	458	-13	453
-18	453	-20	440
-25	464	-24	440
-29	468	-20	462
-33	511	-35	490
-36	534	-44	530
-40	469	-49	630
-46	638	-54	678
-50	766	-60	830
-56	914	-68	1,110
-60	1,090	-76	1,640
-65	1,150		
-70	1,330		
17.9 mg H ₂ O/g ThO ₂			
30	620		
16	670		
11	688		
7	757		
2	755		
-3	795		
-9	904		
-12	1,000		

TABLE 8 - Continued

Temperature, °C	Line Width, cps	Temperature, °C	Line Width, cps
-16	1,040		
-21	1,220		
-24	1,240		
-28	1,360		
-34	1,960		
-37	2,150		
-40	2,690		
<u>Catalyst Th-3</u>		<u>Catalyst Ox-1</u>	
19.5 mg H ₂ O/g ThO ₂		52.9 mg H ₂ O/g ThO ₂	
30	608	30	231
18	584	4	249
14	608	-10	241
10	608	-28	266
4	626	-35	312
0	668	-45	588
-4	635		
-9	691	-27*	232
-15	729	-38*	298
-21	743	-44*	658
-26	794	-49*	1,200
-29	903	-53*	1,590
-34	976		
-38	1,150	*Run 7/12/64; others run 7/10/64	
-42	1,380	43.2 mg H ₂ O/g ThO ₂	
-45	1,480		
-49	1,750		
-54	2,360	-3	254
-57	2,690	-11	254
-62	2,950	-17	244
-67	3,980	-26	249
-70	5,060	-32	270
-74	5,150	-39	327
		-45	806
<u>Catalyst 22-B</u>			
7.9 mg H ₂ O/g ThO ₂			
30	745	-51	1,070
25	742	-55	1,200
16	922	-61	1,440
8	1,120	-67	1,780
3	1,200		
-3	1,380		
-8	1,690		
-13	1,970		
-22	2,170		
		14.0 mg H ₂ O/g ThO ₂	
		30	537
		21	554
		13	497
		8	544
		4	565
		0	587

TABLE 8 - Continued

Temperature, °C	Line Width, cps	Temperature, °C	Line Width, cps
		- 5	609
		-10	629
		-16	728
		-22	792
		-26	847
		-28	930
		-34	1,210
		-38	1,290
		-43	1,350
		-47	1,650
		-52	1,990
		-57	2,700
		-63	3,530
<u>Catalyst Th-5</u>			
26.2 mg H ₂ O/g ThO ₂		14.8 mg H ₂ O/g ThO ₂	
30	319	30	615
21	344	24	628
5	327	19	638
- 1	344	13	644
-10	370	6	654
-18	359	0	659
-24	344	- 6	685
-30	395	-13	702
-36	401	-20	734
-42	441	-25	795
-46	600	-30	850
-50	984	-35	972
-55	1,250	-40	1,040
		-44	1,190
19.6 mg H ₂ O/g ThO ₂		-50	1,390
		-55	1,640
30	425	-60	2,210
14	429		
3	442		
- 3	442		
- 9	436	30	780
-16	458	22	798
-23	468	17	845
-28	482	13	865
-33	485	9	890
-39	526	5	847
-45	654	- 1	885
-50	883	- 5	990
-56	1,190	-10	1,100
-63	1,558	-17	1,160
-70	2,240	-21	1,330

TABLE 8 - Continued

Temperature, °C	Line Width, cps	Temperature, °C	Line Width, cps
		-25	1,420
		-29	1,520
		-34	1,720
		-39	1,950
		-43	2,460
		-49	2,720
		-52	2,750
		-56	3,360

TABLE 9

APPARENT ACTIVATION ENERGIES OF PROCESSES CONTRIBUTING TO THE
SPIN-SPIN RELAXATION OF WATER ON THORIUM OXIDE

Surface Coverage, Using V_m from Water B.E.T.	Apparent Activation Energy, Kcal/mole
<u>Th-1</u>	
0.78	1.26
1.25	1.31
1.57	2.55
<u>Th-3</u>	
1.28	1.74
1.75	1.10
2.21	2.84
<u>Th-5</u>	
1.15	1.18
1.46	1.01
1.94	2.02
2.60	3.79
<u>Ox-1</u>	
1.12	1.63
4.27	4.35
<u>22-B</u>	
0.37	1.45

TABLE 10

CHANGE IN LINE WIDTH OF WATER ADSORBED ON THORIA AFTER
STANDING SEVERAL WEEKS AT A GIVEN SURFACE COVERAGE

Sample	Surface Coverage V/V _m Water B.E.T.	Elapsed Time Between Measurements	Initial Line Width	Line Width at Later Time
<u>Measurements During Adsorption</u>				
22-B	0.57	ca. 2 mos.	398	454
<u>Measurements During Desorption</u>				
Th-1	1.25	65 days	394	393
Th-2	2.65	65 days	396	395
Th-3	1.75	65 days	486	440
Th-5	1.94	65 days	461	448
Th-6	1.65	65 days	432	426
Ox-1	3.48	65 days	252	239
Ox-7-I	2.34	65 days	394	381
Th-2	1.48	50 days	707	692
Th-3	1.28	32 days	624	608
Ox-1	1.96	32 days	379	375
Ox-7-H	2.09	52 days	720	682

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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