Dehydration and Dehydrogenation of 2-Octanol by Thorium Oxide

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The selectivity of 2-octanol reaction by dehydration to octenes *vs.* dehydrogenation to 2-octanone has been determined for thorium oxide prepared by well-defined and reproducible procedures. The selectivity was very dependent on the catalyst pretreatment. In general, thoria pretreated at 600°C with hydrogen was a dehydration catalyst while thoria pretreated at 600°C with oxygen was a more effective catalyst for dehydrogenation. While the pretreatment was the major factor for determining selectivity, the thoria preparative procedure also played a role. The selectivity for 1-octene formation as compared to 2-octene production was also dependent on the pretreatment and on the thoria preparation procedure. Certain thoria preparations were found to be extremely selective for 1-octene formation while others were not very selective. Over some thoria preparations, a large amount of *n*-octane was formed at an early time on stream.

INTRODUCTION

The catalytic conversion of alcohols has been the subject of numerous investigations. Most mechanistic studies have employed alumina as the heterogeneous catalyst and, although great advances have been made, the detailed mechanism is still uncertain *(1, 2)*. Thoria is also a good catalyst for alcohol conversion but it has not been studied to the extent that the alumina catalyst has been. Indeed, even the selectivity of the alcohol conversion—dehydration *vs.* dehydrogenation—has not been firmly established. In a review of dehydration in 1960, Winfield *(3)* wrote: "Enough has been written to make it clear that there are at least three classes of thoria catalyst (nonspecific dehydration, specific dehydration and dehydrogenation), that much of the early work on dehydration over thoria should be repeated with better-defined and reproducible preparations . . ."

For example, Sabatier *(4)* and Balandin, Tolstopyatova, and Dudzik *(5)* found thoria to be a specific dehydration catalyst. On the other hand, Tolstopyatova *(6)* obtained up to 84% hydrogen in the gaseous reaction products from the decomposition of ethanol, a result which indicates a rather selective dehydrogenation catalyst. Hoover and Rideal *(7)* found thoria to give about equal amounts of dehydration and dehydrogenation for ethanol conversion. The present authors *(8)* reported earlier that low area thoria catalyzes *only* dehydrogenation but that dehydration becomes more and more important as the thoria surface area increases. Legg *(9)* observed that thoria, in addition to the simple dehydrogenation and dehydration reactions, converts *n*-propanol and *n*-butanol to the symmetrical alcohol or ketone by the condensation of two alcohol molecules with the concurrent loss of CO and CO_2. Lun-

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deen and Van Hoozer (10) recently reported that thoria had the property of selectively dehydrating 2-ols to the corresponding α-olefins. In contrast, Schappel and Pines (11) found that thoria was more stereospecific for dehydration of decanols than acidic type catalysts (e.g., silica–alumina) but less selective than alumina for dehydration of decanols. This limited survey of the literature clearly demonstrates that the catalytic nature of thoria for alcohol conversion is very poorly defined.

The catalysts used in the above studies, and in most other studies in the literature, were obtained by a variety of preparative procedures. In fact, many of the studies with thoria do not have a sufficiently detailed preparation procedure to justify a valid comparison of the results. In addition, differing pretreatments have been used for the catalysts.

We have made a detailed study of methods for preparing thoria having reproducible surface area (12). The conversion of 2-octanol over catalysts prepared by some of the procedures given in Ref. 12 is the subject of this paper. In addition, an analysis of the olefinic products is important for the understanding of the dehydration mechanism.

EXPERIMENTAL

Catalysts. The general preparative procedures are outlined in Ref. 12. The catalysts used in this study were prepared as a different batch than those used for the surface area study in Ref. 12. However, the catalysts used for the alcohol conversion have the same number and letter designation as used in Ref. 12 with the addition of 2 to represent the second preparation, e.g., catalyst 22-B in Ref. 12 will be referred to as 22-B-2 in this paper.

In the previous investigation of surface areas, the catalyst activation procedure was calcination under vacuum ($\approx 10^{-3}$ Torr) for four hours. In the present study the vacuum treatment was replaced by treatment with oxygen, hydrogen, or nitrogen *in situ* in the reactor. Additional preparative details, as needed, are given in the results section.

Procedure and analyses. The reactor system was of conventional design with a motor-driven syringe liquid feed, Vycor reactor, and sample collector. The LHSV was approximately 0.4 unless otherwise noted. The 2-octanol charge contained approximately 2 mol% 2-octanone. Liquid samples were collected at intervals and the organic liquid layer analyzed by glc using a Carbowax 20M column. The temperature program used for the conversion determinations did not allow a quantitative determination of the individual octene isomers. It was possible to determine quantitatively 1-octene, *trans*-2-octene, and *cis*-2-octene in the absence of 3- and 4-octene isomers by operating the column isothermally at about 60°C. There was no indication of major amounts of other octene isomers in the liquid products. For some runs the individual peaks were trapped and ir and mass spectral analysis showed that the three peaks obtained for these runs were due to 1-octene, *trans*-2-octene, and *cis*-2-octene.

RESULTS

The data in Tables 1–5 show the effect of a hydrogen or oxygen pretreatment on the dehydration: dehydrogenation selectivity for the conversion of 2-octanol over thoria from several preparative procedures.

In Table 1 results are presented for various pretreatments of thoria from the calcination of $Th(NO_3)_4 \cdot 4H_2O$. A large batch of $Th(NO_3)_4 \cdot 4H_2O$ was calcined at 600°C in air; portions of this sample were then pretreated and used for the runs in Table 1. Samples pretreated with hydrogen were very selective dehydration catalysts; the amount of the dehydrogenation product, 2-octanone, just corresponds to the 2-octanone impurity in the 2-octanol charge. Pretreatment with hydrogen saturated with water (25 mm) may have reduced the activity slightly but the selectivity was identical to the hydrogen pretreated sample. A sample pretreated with oxygen at 600°C, then cooled to reaction temperature in oxygen, initially catalyzed about equal amounts of dehydration and dehydrogenation; the

TABLE 1

CONVERSION OF 2-OCTANOL OVER THORIA FROM THE THERMAL DECOMPOSITION OF THORIUM
NITRATE HYDRATE (LHSV = 0.4, 250°C, NO CARRIER GAS)

Catalyst	Liquid Collected, (cc)	Time on Stream (min)	Mol% of Liquid Products[a]			Activation Pretreatment
			n-Octane	Octenes	Octanone	
25Z[b]	0.4	42	20	64	0.8	Three Hours in H_2 at 500°C,
	1.3	84	2.9	53	2.4	cool in H_2
	1.5	129	2.2	48	1.7	
	1.6	185	2.1	44	2.1	
25-G-2	0.4	43	29	52	2.1	Three Hours in H_2 at 550°C,
	1.4	86	7.9	53	3.4	cool in H_2
	1.5	134	6.1	50	4.9	
	1.8	190	4.7	44	4.1	
25-Z	0.4	50	23	33	2.0	Three Hours in H_2, then 1/2
	1.0	84	5.6	24	2.2	Hour with water (25 mm)–
	1.2	124	4.0	20	2.3	H_2 Mixture, cool in Mixture
25-Z	0.6	95	trace	33	3.2	Three Hours in O_2, 15 Min.
	1.8	155		29	3.0	in N_2 at 600°C, Cool in N_2
	1.6	210		24	3.7	
	1.1	243		23	2.7	
	0.6	65		14	16	Above Sample in O_2 at
	1.7	125		5.4	14	600°C, Cool in O_2
	1.3	175		4.2	14	
	0.6	70	trace	41	1.0	Above Sample with above O_2–N_2 Treatment

[a] Mol% of liquid products neglecting water as a product.

[b] Similar to 25-G except the sample was heated to 600°C in air over a one hour period without half-hour heating at intermediate temperatures as used for 25-G. The surface area after air calcination was about 30 m^2/g.

dehydration activity rapidly declined with time on stream but the dehydrogenation activity remained nearly constant. The oxygen responsible for the dehydrogenation activity must not be tightly bound to this particular thoria sample. A sample of 25-Z was heated at 600°C in oxygen, then flushed at 600°C for 15 minutes with nitrogen, and cooled to the reaction temperature in nitrogen; this sample was very selective for dehydration (AA' of the selectivity curve in Fig. 1). This sample was then treated *in situ* for 16 hr in oxygen and cooled to reaction temperature in oxygen; the sample was now more active for dehydrogenation than dehydration (BB' in Fig. 1). Repeating the oxygen pretreatment followed by a nitrogen flush at 600°C again yielded a se-

lective dehydration catalyst (point C, Fig. 1).

Thoria obtained by thorium oxalate calcination gave similar selectivity results. The hydrogen pretreated catalyst was very selective for dehydration; the oxygen pretreated sample was more active for dehydrogenation than for dehydration. The temperature (400, 550, or 600°C) of the oxygen pretreatment does not seem to alter the catalyst selectivity for dehydration:dehydrogenation (Table 2).

Results are presented in Table 3 for the conversion of 2-octanol over thoria obtained by heating three other materials: the carbonate, the oxalate–hydroxide complex, and the hydrous oxide precipitated using isopropyl alcohol rather than water as the
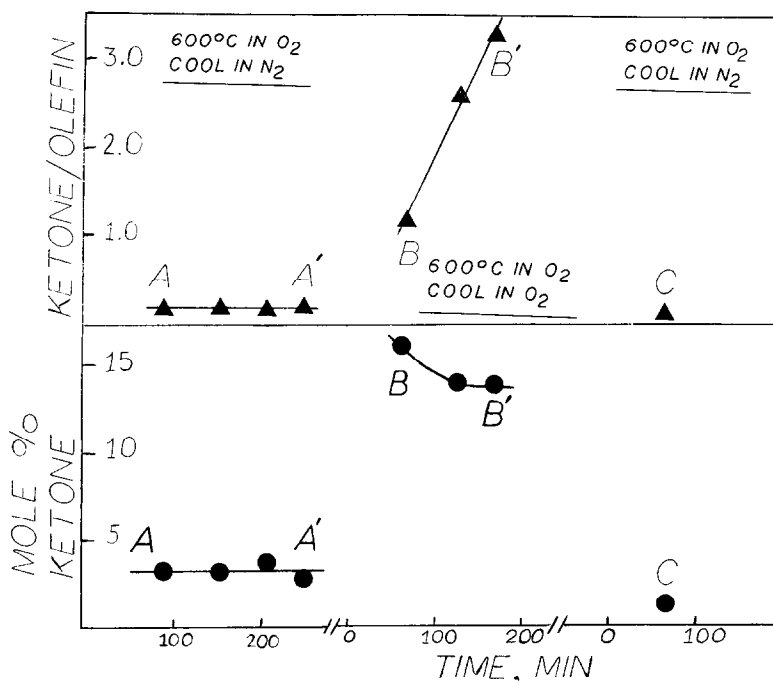
FIG. 1. Influence of pretreatment on the dehydrogenation activity and ketone/olefin selectivity for 2-octanol conversion. (At point A' the catalyst was treated overnight at 600°C in oxygen and cooled in oxygen; at point B' the catalyst was treated overnight at 600°C in oxygen and then cooled to reaction temperature in nitrogen.)

solvent. All three thoria preparations show that the hydrogen pretreatment resulted in a dehydration catalyst while calcination in oxygen produced a catalyst active for dehydrogenation. The oxygen-treated thoria from the carbonate (40-1) and from the hydroxide–oxalate (22-B-2) shows practically no dehydration activity but a high conversion to the dehydrogenation product, 2-octanone.

A sample from the isopropyl alcohol precipitation was calcined in oxygen before the three-hour hydrogen treatment at 600°C; this sample showed both dehydration and dehydrogenation activity. This indicates that the oxygen is more difficult to remove from this sample than from thoria obtained from thorium nitrate calcination where the dehydrogenation activity was decreased by merely flushing with nitrogen at 600°C. Furthermore, the hydrogen pretreatment of the calcined thoria from the thorium carbonate was sufficient to eliminate the dehydrogenation activity. Thus, the ease of removal of the oxygen

responsible for the dehydrogenation activity depends on the source of thoria; the ease of removal is thoria from $Th(NO_3)_4$ calcination > carbonate > isopropyl alcohol precipitation.

Results for conversion of 2-octanol over thoria obtained from precipitation by adding ammonium hydroxide to thorium nitrate solutions of various concentrations are presented in Table 4. All of these thoria catalysts were selective dehydration catalysts when a hydrogen pretreatment was used. Using this precipitation procedure the surface area reaches a maximum as the thorium concentration is decreased from 1.8 to 0.3 M; a further decrease of the thorium concentration results in a corresponding decrease of the thoria area. In Fig. 2 the 2-octanol conversion for hydrogen pretreated samples are shown as a function of the Th^{4+} concentration of the solution used for the precipitation. Thus, it appears that the minimum conversion occurs over the thoria sample which had the highest surface area.

TABLE 2

CONVERSION OF 2-OCTANOL OVER THORIA OBTAINED FROM THORIUM OXALATE
(LHSV = 0.4, 250°C, NO CARRIER GAS)

Catalyst	Liquid Collected, (cc)	Time on Stream, (min)	Mol% of Liquid Products[a]					
			n-Octane	Octenes	Octanone	A[b]	B[b]	C[b]
Hydrogen Pretreatment								
7-X[c]	0.5	60	1.2	49	5.3			
	1.4	110	traces	25	6.6			
	1.6	162		21	6.9			
	1.0	195		20	7.3			
Oxygen Pretreatment								
7-Y-1[d]	0.4	65	12	24	33	3.4	2.3	1.7
	1.2	127	2.8	17	34	2.8	2.3	2.3
	1.4	183	1.6	12	33	1.8	1.2	2.3
	1.6	240	1.1	9	32	1.6	0.9	1.7
7-Y-2[e]	0.4	51	trace	10	20	traces only		
	1.3	94		6.3	17			
	1.4	136		4.2	15			
	2.0	208		3.9	13			
7-Y-3[f]	0.5	51	trace	8.6	14	traces only		
	1.0	88		8.0	13			
	1.2	123		6.4	12			
	1.2	164		4.3	12			

[a] Mol% liquid products not including water.
[b] Three unidentified products eluting 2–5 min after 2-octanol.
[c] Calcine at 600°C in air for 14 hr, then 3 hr in hydrogen at 550°C.
[d] 16 g thorium oxalate hydrate calcined in oxygen at 550°C for 3 hr.
[e] 5.6 g thorium oxalate hydrate calcined in oxygen at 600°C for 3 hr; LHSV ≈ 1.2.
[f] 4.5 g thorium oxalate hydrate calcined in oxygen at 400°C for 3 hr; LHSV ≈ 1.4.

The oxygen pretreatment for catalyst 9 series did not give a simple trend, particularly with respect to the dehydration activity as the thorium concentration was varied. This irregularity may be a real phenomenon or it may be that the processes occurring during activation are very complicated and were not sufficiently controlled during this exploratory study. The sample from 1.8 M Th^{4+} had dehydration activity, the sample from 0.9 M concentration was inactive, a further decrease to 0.06 M produced an active catalyst while the sample from 0.03 M concentration was inactive. The dehydrogenation activity was more consistent: all the catalysts except the two from the very dilute Th solutions (0.06 and 0.03 M) were active for dehydrogenation. In this series, the least active catalyst for dehydration when treated with hydrogen was the most active dehydrogenation catalyst when treated with oxygen.

Thoria prepared by precipitation from an 0.6 M thorium chloride solution was much more active for dehydration than any of the other catalysts we used. The results in Table 5 were obtained after the temperature was decreased to 200°C and the LHSV increased to 0.5. In contrast to the other thoria sources, these samples pretreated with either hydrogen or oxygen had about the same selectivity. This may be due to a low dehydrogenation activity at 200°C.

In many runs a considerable amount of n-octane was formed. The n-octane peak was trapped from the glc effluent and its identity was confirmed by a mass spectrum. The n-octane appears to be formed in appreciable quantities only over the hydrogen

TABLE 3

CONVERSION OF 2-OCTANOL OVER THORIA OBTAINED FROM VARIOUS PREPARATIVE PROCEDURES
(LHSV = 0.4, 250°C, NO CARRIER GAS)

Catalyst	Time on Stream, (min)	Mol% of Liquid Products[a]			Time on Stream, (min)	Mol% of Liquid Products[a]		
		n-Octane	Octenes	Octanone		n-Octane	Octenes	Octanone
		Hydrogen Pretreat, 600°C				*Oxygen Pretreat, 600°C*		
24-B-2[b]	52	1.7	38	3.9	65	—	10	14
	93	0.9	32	3.6	104	—	7.3	11
	125	1.0	30	3.4	136	—	5.2	8.6
	175	0.5	26	4.0				
24-B-2[c]	57	35	51	5.9				
	95	15	33	14				
	144	10	26	11				
	189	7.2	22	10				
	237	6.1	20	9.2				
40-1[d]	65	23	43	1.1	62	—	4.1	19
	111	trace	23	1.7	109	—	2.9	13
	160		21	1.2	148	—	1.9	11
	202		21	2.0				
40-1[e]	55	4.3	60	1.1				
	102	trace	42	1.7				
	145		34	1.4				
	190		27	1.8				
	231		27	2.1				
22-B-2[f]	48	1.7	22	2.9	78	—	3.7	31
	85	—	15	2.2	134	—	1.0	20
	128	—	13	1.9	186	—	trace	18
					224	—	trace	16

[a] Mol% of liquid products excluding water.

[b] Precipitated from an isopropyl alcohol solution of thorium nitrate with ammonium hydroxide.

[c] Heat at 550°C in oxygen for 14 hr, then 3 hr at 600°C in hydrogen.

[d] Hydrogen or oxygen pretreatment of thorium carbonate at 600°C.

[e] Thorium carbonate calcined in air at 600°C, then in hydrogen for 3 hr at 500°C.

[f] Hydrogen or oxygen pretreatment of the thorium oxalate–hydroxide complex at 550°C.

pretreated samples and only at early times on stream.

Tables 6 and 7 present data for the other type of selectivity: the ratio of 1-octene: 2-octene and the cis:trans-2-octene ratio. In Table 6 the olefin distribution is shown for catalyst series 9. This selectivity varied with catalyst preparation. For the hydrogen pretreated catalysts, the catalyst most selective for α-olefin* was the one precipitated from the 0.6 M thorium solution. It also

* We refer to selectivity for α-olefin formation even though all catalysts may form only α-olefins and the other octene isomers may arise from the isomerization of 1-octene.

appears that the least selective catalysts for α-olefin formation were the ones that formed the most n-octane (see Tables 4 and 6). The amounts of cis- and trans-2-octene formed were nearly equal except for the 1.8 M precipitation material. The most selective catalyst was one that was heated at 600°C in the reactor without a flow of any gas. 1-Octene comprised 96–100% of the dehydration product; furthermore, the catalyst, although exposed to oxygen at 600°C, gave little dehydrogenation to 2-octanone and formed only traces of n-octane.

Catalysts prepared by other procedures

TABLE 4

CONVERSION OF 2-OCTANOL OVER CATALYST SERIES 9 (THORIA FROM PRECIPITATION FROM THE NITRATE SOLUTION WITH AMMONIUM HYDROXIDE; LHSV = 0.4, 250°C, NO CARRIER GAS)

Catalyst	Time on Stream, (min)	Mol% of Liquid Products[a]			Time on Stream, (min)	Mol% of Liquid Products[a]		
		n-Octane	Octenes	Octanone		n-Octane	Octenes	Octanone
		Hydrogen Pretreat, 600°C				Oxygen Pretreat, 600°C		
9-K-2	35	5.2	95	—	60	—	13	13
	90	2.0	94	4.0	95	—	10	10
	141	1.3	85	8.5	150	—	3.3	13
	186	2.4	76	9.7	175	—	trace	13
9-M-2	62	4.7	27	5.2	60	—	traces	24
	120	0.8	22	7.5	105	—	"	18
	171	—	13	4.5	190	—	"	16
	218	—	17	5.5	232	—	"	11
9-N-2	62	4.4	55	1.6	56	—	18	7.2
	120	0.5	40	1.6	113	—	9.5	7.2
	177	—	41	2.3	168	—	11	5.8
	216	—	36	2.6	208	—	11	6.1
9-A-2	43	2.2	59	1.1	62	—	16	0.7
	93	—	45	1.0	132	—	14	2.1
	141	—	42	2.2	190	—	14	1.8
	190	—	35	2.8	237	—	11	1.6
	237	—	35	2.0				
9-D-2	50	6.3	56	7.3	53	—	6.1	3.0
	95	3.3	38	9.3	113	—	2.8	2.8
	95	3.3	38	9.3	113	—	2.8	2.8
	155	4.0	39	8.6	193	—	2.2	2.9
	204	2.5	34	9.6				
9-E-2	45	5.5	58	3.2	58	—	20	3.5
	93	2.4	41	3.4	111	—	19	4.7
	138	2.0	35	3.5				
	200	1.9	34	3.2				
	232	0.6	26	1.9				

[a] Mol% of liquid products excluding water.

also showed a wide range of selectivity for α-olefin formation (Table 7). The results for 25-Z, the catalyst from thorium nitrate decomposition, are interesting. When 25-Z was treated at 600°C in oxygen, then flushed with nitrogen at 600°C, and cooled to the reaction temperature in nitrogen, it was selective for α-olefin formation. After this catalyst was then heated to 600°C in oxygen and cooled to the reaction temperature in oxygen it was not selective for α-olefin formation. When 25-Z was pretreated in hydrogen the catalyst was not selective for α-olefin formation; in addition, it catalyzed the formation of a large quantity of n-octane.

For several of the catalysts the amount of the α-olefin was increasing with time so that, at long time on stream, these catalysts might become selective for α-olefin formation.

DISCUSSION

The results make it clear that the dehydration and dehydrogenation selectivity was primarily determined by the catalyst pretreatment. A catalyst pretreated at 500–
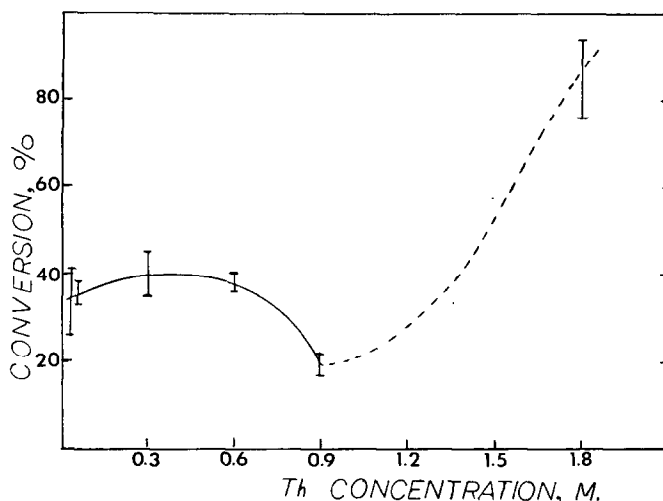
Fig. 2. Conversion of 2-octanol over thoria obtained by precipitation from solutions of various Th^{4+} concentrations.

600°C in hydrogen was a good dehydration catalyst but had only slight, if any, dehydrogenation activity. On the other hand, a catalyst pretreated in oxygen produced a material which was usually more active for dehydrogenation than for dehydration; furthermore, the dehydration activity of this sample declined more rapidly than the dehydrogenation activity. This catalyst selectivity was acquired at the high-temper-

TABLE 5

DEHYDRATION OF 2-OCTANOL OVER THORIA
PRECIPITATED FROM THORIUM CHLORIDE
(LHSV = 0.5, 200°C, NO CARRIER GAS)

Time on Stream, (min)	Liquid Collected, (cc)	Mol% of Liquid Products[a]		
		n-Oc-tane	Octenes	Oc-tanone
Hydrogen Pretreatment, 600°C				
58	0.4	—	32	1.0
96	1.0	—	36	1.0
158	1.8	—	37	2.5
224	2.4	—	38	1.4
Oxygen Pretreatment, 600°C				
80	0.5	—	57	9.8
114	1.0	—	47	5.5
175	1.5	—	46	3.3
226	1.4	—	36	3.0

[a] Mol% of liquid products excluding water.

TABLE 6

OLEFIN DISTRIBUTION FROM 2-OCTANOL
DEHYDRATION OVER CATALYST SERIES 9
(SEE TABLE 4 FOR CONVERSION
AND RUN CONDITIONS, DATA
GIVEN IS FOR THE HYDROGEN
PRETREATED CATALYSTS)

Catalyst	Sample	Mol% of Olefins[a]		
		1-Oc-tene	*trans*-2-Octene	*cis*-2-Octene
9-K-2	1	51	35	14
	2	42	39	19
	4	44	38	18
9-M-2	1	55	24	21
	2	67	16	17
	4	67	16	17
9-M-2[b]	1	96	4.4	
	2	99	1.0	
	4	99	traces	
9-N-2	1	63	23	14
	2	63	21	16
	5	65	21	14
9-D-2	1	35	28	37
	4	36	27	37
9-E-2	1	38	31	31
	5	36	32	32

[a] Samples are omitted when the olefin distribution was not changing with time.

[b] Sample activated without a gas flow.

TABLE 7

OLEFIN DISTRIBUTION FOR THE DEHYDRATION OF 2-OCTANOL OVER THORIA FROM VARIOUS PREPARATIONS (CONVERSION FOR A PARTICULAR RUN IS GIVEN IN TABLES 2–5)

Thoria source	Pretreatment	Sample	Mol% of olefins[a]		
			1-Octene	trans-2-Octene	cis-2-Octene
Thorium Nitrate (25-Z)	Oxygen at 600°C, then N₂ at 600°C	1	72	16	12
		2	82	9	9
		4	86	7	7
(25-Z)	Oxygen at 600°C	5	34	36	30
(25-Z)	Hydrogen at 600°C	1	31	32	37
		2	44	31	25
		3	50	26	24
Thorium Oxalate	Hydrogen at 600°C	2[b]	51	27	22
		3	70	14	16
		4	72	12	16
Thorium Oxalate	Oxygen at 600°C	1	39	33	28
		4	43	27	30
22-B-2	Hydrogen at 600°C	1	60	19	21
		3	73	13	14
Th(CO₃)₂	Hydrogen at 600°C	2[b]	74	12	14
		3	82	10	8
Th(CO₃)₂	Hydrogen at 550°C	1	66	20	14
		2	76	12	12
		3	85	7	8
		4	86	7	7
24-B-2	Hydrogen at 600°C	1	52	25	23
		4	51	22	27
ThCl₄[c]	Hydrogen at 600°C	1	24	28	48
		4	25	30	45

[a] Samples are omitted when the olefin distribution was not changing with time.
[b] The first sample was not analyzed.
[c] Run at 200°C; other runs at 250°C.

ature treatment (400–600°C); for example, a sample pretreated in oxygen at 600°C followed by three hours heating in flowing hydrogen at 250°C had a catalytic selectivity similar to a catalyst treated with only oxygen at 600°C. But, if this hydrogen treatment was at 600°C the selectivity was altered.

In addition to pretreatment, the catalyst preparation played a role in determining the selectivity. Since the difference in selectivity for many preparations was not nearly as great as that produced by pre-

treatment, the decline in catalytic activity of the thoria under our experimental conditions make detailed comparisons difficult.

As is evident from Table 4 and Fig. 2, the concentration of the thorium solution used for precipitation influences activity. In general, the samples of higher surface area appear to be less active than those of intermediate surface area. The most active dehydration sample was obtained from a very concentrated thorium solution (1.8 M; ≈50 wt%); one from an 0.9 M thorium solution was less active, but with further

dilution the activity increased to a nearly constant value. This activity trend has also been observed with alumina (*13*) where the conversion initially increased with increasing area but a maximum activity–area ratio was reached, so that further area increases resulted in lower conversion per unit surface area.

The heterogeneous catalysts that show both dehydrogenation and dehydration activity in alcohol conversion are usually semiconductors. Even for semiconductors, there are contrasting theories to explain the catalyst selectivity. Vol'kenshtein's electronic theory of catalysis on semiconductors (*14*) requires a decrease in dehydrogenation activity for a lowering of the Fermi level while raising the Fermi level would increase the amount of dehydrogenation. On the other hand, Hauffe (*15*) presents a theory that predicts that lowering the Fermi level would increase the rate of dehydrogenation. Thus, while the theories disagree in the direction of selectivity change by altering the Fermi level, they do attribute changes in the Fermi level as being responsible for the selectivity.

However, thoria is usually not considered to be a typical semiconductor. Dowden (*16*) classifies ThO_2 as an ionic insulator. Also, thoria has not been reported to exist in various oxidation states. Recent studies by Breysse (*17*) have shown that the treatment of thoria with hydrogen or oxygen at 500°C causes a very slight variation, *if any*, from the stoichiometry of ThO_2. This would suggest that the selectivity differences we observed with hydrogen or oxygen pretreatment cannot be attributed to typical bulk semi-conductor properties, but must be due to differences in the "surface" layer. It would thus appear that treatment of thoria at 600°C with hydrogen must remove some surface oxide ions leaving an excess of Th ions in the surface layer. Likewise, pretreatment with oxygen would provide a surface with excess "oxygen" ions. This postulate, in effect, allows thoria to acquire the surface properties of a semiconductor even though bulk thoria would be an ionic insulator. Thus, a thoria surface deficient in oxygen ions would be an active dehydration catalyst while one with excess oxygen ions would be an active dehydrogenation catalyst.

It must be kept in mind that the thoria we used for the catalytic studies may be quite different from the very pure, low area thoria normally used for conductivity studies. Thoria obtained by preparation from thorium nitrate by decomposition or precipitation may not be an insulator because of anionic impurities. We have found that thoria prepared from the nitrate exhibits a complicated EPR spectrum (*18*) even though pure ThO_2 should not have an EPR spectrum. This EPR signal is destroyed only after heating thoria to 900–1000°C; at this temperature oxides of nitrogen are liberated and the high surface area is lost. However, the EPR signal did not appear to be different when the thoria was heated at 600°C in vacuum, hydrogen, or oxygen. Thoria from other preparative procedures used in this study also gave EPR signals. Only a very pure, low area thoria or a thoria sample heated to about 1000°C did not produce an EPR signal. In this connection, Breysse (*17*) reported that thoria from the oxalate was a *n*-type semiconductor but thoria from the nitrate was a *p*-type semiconductor.

A final choice of the electronic properties of thoria which determine the selectivity for alcohol conversion must await more detailed study of the thoria itself. On the other hand, our results make it apparent that the selectivity is dependent on the surface of thoria and that dehydrogenation and dehydration must occur on different active sites. This suggests that the various selectivity properties of thoria observed by earlier workers—dehydration only, both dehydration and dehydrogenation, and dehydrogenation only—were due in part to the catalyst pretreatment. For instance, evacuation or heating in an inert gas would result in a surface that could have both oxygen-deficient and oxygen-excess "patches" on the surface and be active for both dehydration and dehydrogenation. In addition, the high area thoria, when treated with oxygen, is more selective for dehydrogenation than a similarly treated low area thoria.

The chemical reaction between the alcohol and chemisorbed oxygen

$$R_2CHOH + O_{(ads)} \rightarrow R_2C{=}O + H_2O,$$
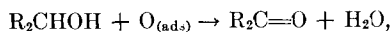
was considered as a possible alternative for the dehydrogenation activity. However even if oxygen is adsorbed with the molecular axis perpendicular to the surface, there is insufficient oxygen in a monolayer to account for the amount of 2-octanone formed. Thus, the adsorbed oxygen must act as a center of catalytic activity.

In many runs, significant amounts of n-octane were obtained. In these runs only small amounts of octanone were obtained so it would not appear that the hydrogen transfer from alcohol to olefin to form n-octane and 2-octanone was occurring. It seems more likely that n-octane was formed by hydrogenation by adsorbed hydrogen atoms. It is possible that this resulted from a reaction of the surface initially deficient in oxygen with the alcohol to give hydrogen, as atoms or ions, accompanied by retention of oxygen from the alcohol by the surface to reduce the oxygen deficiency. This is supported by the fact that n-octane was formed in large amounts early in the reaction but rapidly decreased with time on stream.

The second type of selectivity observed with thoria is the distribution of the 1- and 2-olefins from 2-octanol. It has been reported by Lundeen and Van Hoozer (10) that thoria (and other lanthanide metal oxides) are very selective for the formation of α-olefins from 2-ols. This selectivity is much different than that usually found for dehydration over alumina (1) or in solution (19) and in gas phase elimination reactions (20). Lundeen and Van Hoozer proposed a cyclic six-atom intermediate similar to that proposed for gas phase pyrolysis

It was further proposed that structures II and III leading to 2-octenes are less likely than I due to lower stability because of steric interactions and that a larger part of the alcohol molecule is close to the catalyst surface.

It is difficult to understand why an aluminum oxide surface, on which 2-ols eliminate water to give both 1- and 2-olefins, would not have the same steric interaction limitations for structures II and III. But for those elimination reactions where the Hoffman elimination to 1-olefin is favored, the most widely accepted explanation is that the hydrogens β to the carbon with the "charge center" acquire a partial positive charge (20). Alkyl groups, in the present case the pentyl group, are electron-releasing and this decreases the charge on the hydrogens in the β-CH_2 group relative to that on the β-CH_3 group. It seems more reasonable that this sort of electronic effect, rather than a steric effect, is the cause of the different selectivity. If the oxygen ion in thoria is less "basic" than one in alumina, then the weaker base would be more likely to eliminate water using the hydrogen with the highest positive charge (i.e., acidity). That is to say, the weaker "oxygen ion" base will be more likely to react with the more acidic hydrogen in the β-CH_3 than the CH_2 β to the OH-containing carbon. The stronger the "oxygen ion" base the less dependent the selectivity is on the charge (or acidity) developed on the CH_3 or the CH_2 group. Thus, we would expect different catalysts to produce 1- and 2-olefins in continuously varying ratios rather than as exclusive products.

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I   II   III
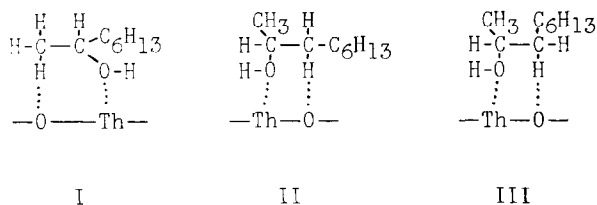
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