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Dehydrocyclodimerization

III. Dehydrocyclodimerization of Butanes over Transition Metal Oxide Catalysts

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Dehydrocyclodimerization converts light paraffins to aromatics over catalysts with dehydrogenation and acid components. Because dehydrocyclodimerization catalysts require frequent regeneration, transition metal oxides might be preferred over Pt-containing catalysts. We tested supported oxides of Cr, V, Mo, W, and Mn. The vanadium oxide–alumina catalyst performed better at all pressures than the other catalysts.

Light paraffins are converted to aromatics in dehydrocyclodimerization. Reactions of butanes (*1*), propane, and pentane (*2*) over supported platinum catalysts were described previously. Because dehydrocyclodimerization catalysts must be regenerated quite frequently, transition metal oxide catalysts, which can be regenerated many times without losing activity might be preferred over platinum-containing ones. Here we describe dehydrocyclodimerization of butanes over transition metal oxides.

EXPERIMENTAL METHODS

Reaction conditions, analytical procedure, and the hydrocarbons used were as described before (*1*). The nonacidic chromia–alumina was similar to the one used by Pines and Chen (*3*). The acidic chromia–alumina was prepared by impregnating Davison eta-alumina with a solution of CrO_3. The dried catalyst was calcined for 2 hr at 480°C in N_2. Oxides of Mo, V, W, and Mn on alumina (4% metal in each case) were similarly prepared on Davison eta-alumina by impregnation with solutions of $(NH_4)_6Mo_7O_{24}4H_2O$, VCl_3, H_2WO_4, and $Mn(NO_3)_2$. Vanadium oxide on neutralized alumina (4% V and 0.2% K, as oxides) was prepared by impregnating alumina with a solution of KNO_3 and VCl_3. Fluorided aluminas (1.3, 3.3, or 5.5% F) were prepared by impregnating eta-alumina with aqueous HF solutions.

RESULTS AND DISCUSSION

Chromia–Aluminas

Table 1 shows *n*-butane dehydrocyclodimerization results over acidic and neutralized chromia–aluminas. Over the neutralized (0.1% K) chromia–alumina, conversion to aromatics is low (1 to 3 wt %). More ethylbenzene is found in the C_8 aromatics than expected from equilibrium. The predominant aromatic products with isobutane are *p*-xylene and toluene. Skeletal isomerization is very limited: With *n*-butane, the isobutylene/*n*-butenes ratio is around 0.02. Butane conversions to aromatics over acidic chromia–alumina or mixtures of neutralized chromia–alumina and various solid acids are between five and nine times higher than over neutralized chromia–alumina alone (Tables 1 and 2 and Fig. 1).

With mixtures of neutralized chromia–alumina and solid acids, conversions to aromatics are higher and recycle yields are better with eta-alumina or fluorided eta-alumina than with silica–alumina as the

TABLE 1

Dehydrocyclodimerization of *n*-Butane over Chromia–Alumina at an LHSV of 1 at Atmospheric Pressure[a]

Catalyst composition: Cr (wt %):	32		5.5	
K (wt %):	0.1		0	
Reaction temp (°C):	560	593	560	593
Product composition (wt %)				
n-Butane	49.9	25.5	23.3	6.0
Isobutane	0.6	1.0	6.6	3.3
Butenes	38.6	41.1	19.8	12.1
Butadiene	2.06	3.6	0.5	0.5
Pentenes	0.1	0.2	0.6	0.1
Methane	1.0	3.8	6.5	12.8
Ethane, ethylene	2.2	9.4	11.5	21.4
Propane	1.08	4.0	12.1	12.3
Propylene	1.2	3.4	4.9	6.7
Benzene	0.14	0.54	1.54	2.9
Toluene	0.12	0.46	2.19	3.1
Ethylbenzene (and xylenes)	0.8	2.0	5.04	5.1
C_9 Aromatics	—	—	1.38	1.7
Coke	0.6	3.0	3.0	10.9
Hydrogen	1.6	1.9	1.05	1.1
Ultimate recycle yield of aromatics (wt %)	16	14	32	22
Isobutylene/*n*-butenes	0.02	0.05	0.45	

[a] Catalysts are regenerated after each experiment with a 1:1 air:nitrogen mixture. A hydrogen treatment of at least 30 min follows each regeneration at the temperature of the next experiment. Data is for regenerated catalyst.

acid component (Table 2). Optimum fluoride concentration is between 1.3 and 2 wt % (Figs. 2 and 3). Coking is less over fluorided alumina mixtures than over mixtures with the other solid acids.

Temperature effects were studied with the acidic chromia–alumina and are shown in Fig. 4. Conversions to aromatics, methane–ethane–ethylene, and coke increase with increasing temperature between 490 and 600°C. The highest single-pass conversion to aromatics (12.8%) was obtained at

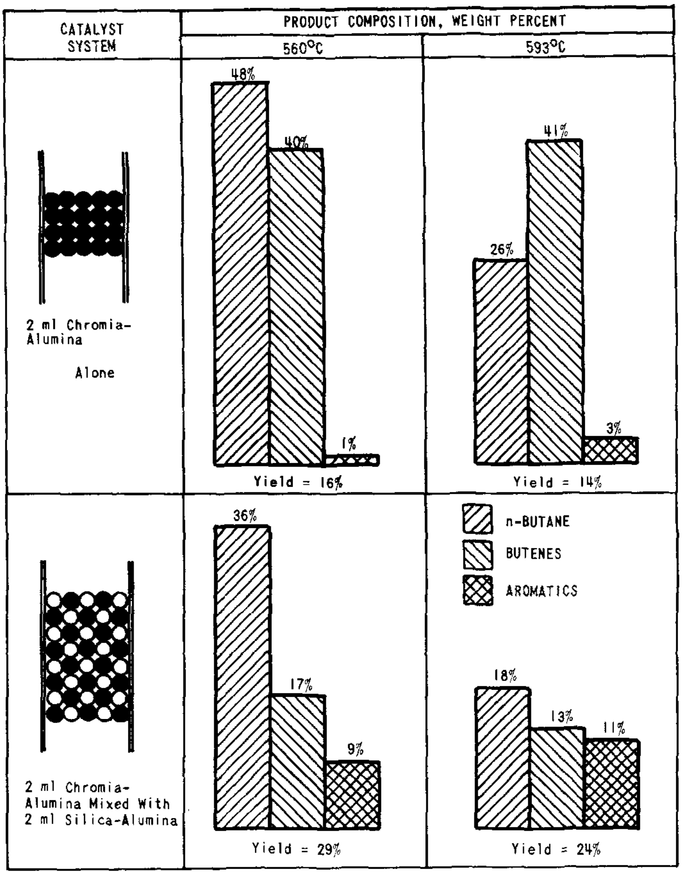
TABLE 2

Dehydrocyclodimerization of *n*-Butane over Mixtures[a] of Nonacidic Chromia–Alumina (0.1% K) and Solid Acids at 593°C, and at Catalyst Onstream Times of 1 min

Acid component:	Eta-alumina		Eta-alumina		Fluorided alumina (1.3% F)	Fluorided alumina (3.3% F)		Silica-alumina	
Chromia–alumina/acid ratio:	2:1		1:1		2:1	2:1		1:1	
LHSV:	0.6	1	0.5	0.8	1	0.6	1	0.5	0.5[b]
Product composition (wt %)									
Butenes	4.3	15.2	1.1	6.3	5.1	4.1	7.2	13.0	14.3
Total aromatics	27.4	18.7	27.8	20.8	23.5	19.9	13.6	15.3	14.4
Coke	7.1	7.8	8.2	7.2	3.8	3.5	4.3	9.9	10.9
Ultimate recycle yield of aromatics	42	39	37	41	41	35	37	33	35

[a] Physical mixtures of 20/60 mesh size particles.

[b] Isobutane feed.



(Reaction Conditions: Atmospheric Pressure, 1.9 ml Liquid Feed/Hour Flow Rate, and 3 Minutes Catalyst Onstream Time)

Fig. 1. Dehydrocyclodimerization of *n*-butane over chromia-alumina and a 1:1 mixture of chromia-alumina and silica-alumina.

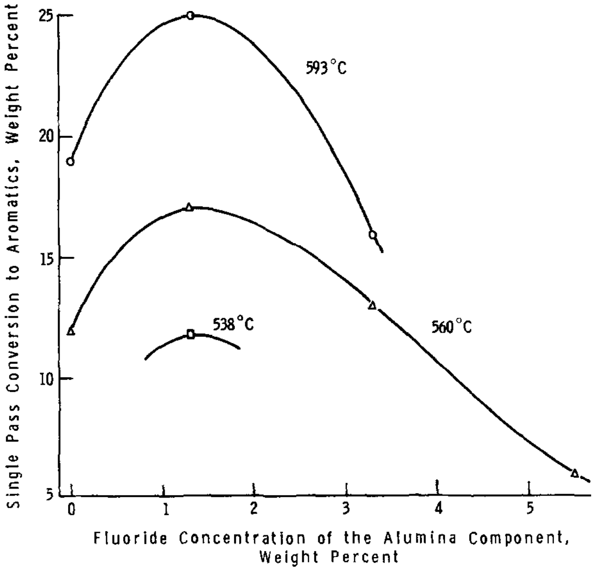


Fig. 2. Dehydrocyclodimerization of *n*-butane over mixtures of chromia-alumina and fluorided aluminas (chromia-alumina/fluorided alumina ratio = 2:1).

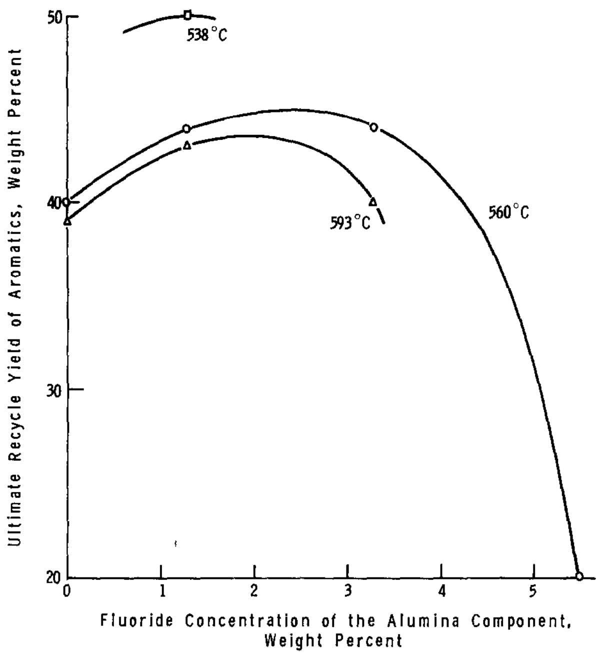
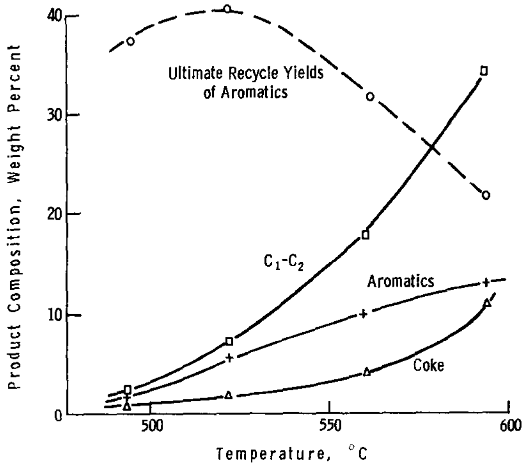


FIG. 3. Dehydrocyclodimerization of *n*-butane over mixtures of chromia-alumina and fluorided aluminas.

593°C. Ultimate recycle yield is highest at about 520°C (41 wt %).

Figures 5 and 6 show examples of the effects of catalyst onstream time. Yields, conversions to aromatics, and overall butane conversions decrease with increasing catalyst onstream times. Results with *n*-butane and isobutane are similar. A typical distribution of the different aromatics formed over a mixture of neutralized chromia-alumina and silica-alumina at 560°C is: 10 wt % benzene, 18% toluene, 51% C_8, and 21% C_9 and higher aromatics. Xylenes and ethylbenzene are at their equilibrium



Sampling Time = 2 Minutes

FIG. 4. Dehydrocyclodimerization of *n*-butane over acidic chromia-alumina at 1 atm pressure. Effect of temperature.

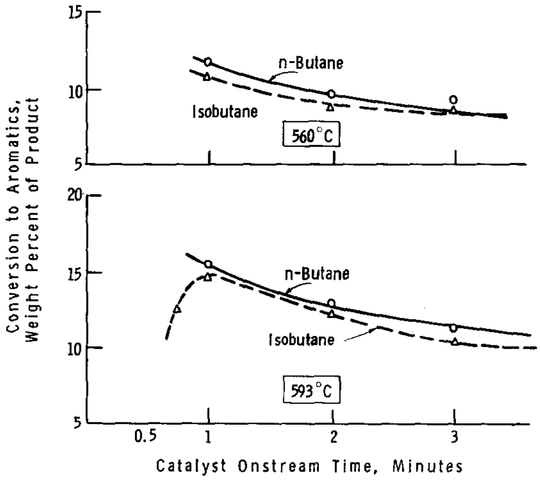


FIG. 5. Dehydrocyclodimerization of butanes: effect of catalyst onstream time on conversions to aromatics; catalyst: 1:1 mixture of chromia-alumina and silica-alumina; pressure = 1 atm; LHSV = 0.5.

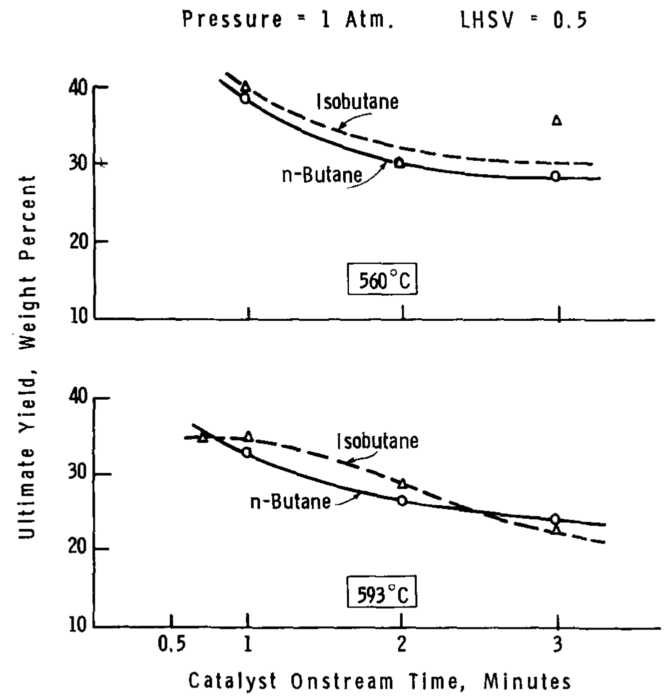


FIG. 6. Dehydrocyclodimerization of butanes: effect of catalyst onstream time on ultimate recycle yields of aromatics; catalyst: 1:1 mixture of chromia-alumina and silica-alumina; pressure = 1 atm; LHSV = 0.5.

TABLE 3

DEHYDROCYCLODIMERIZATION OF *n*-BUTANE OVER DIFFERENT TRANSITION METAL OXIDE CATALYSTS[a] AT 560°C, 1 ATM, AND A LHSV OF 0.96

Oxide:	Molybdenum	Vanadium	Tungsten	Chromium	Manganese
Total aromatics (wt %)					
At 2 min onstream time	18.2	17.2	7.2	9.7	1.0
At 10 min onstream time	11.6	10.6	4.2	5.8	—
Yield (wt %)[b]					
At 2 min onstream time	33	43	24	28	20
At 10 min onstream time	29	30	21	18	—
Coke (wt %)[c]					
At 2 min onstream time	8.1	3.8	5.2	3.5	0.4
At 10 min onstream time	8.0	7.6	4.2	8.8	—
Isobutylene/*n*-butenes					
At 2 min onstream time	0.6	0.6	0.6	0.46	

[a] Impregnated on 16/32 mesh eta-alumina. Metal content is about 4 wt %.

[b] Yields are calculated assuming that all C_3-C_4-C_5 hydrocarbons are recycled.

[c] Coke is calculated from the CO_2 content of the regeneration offgases.

TABLE 4

DEHYDROCYCLODIMERIZATION OF n-BUTANE OVER VANADIUM CONTAINING CATALYSTS AT 593°C WITH AN LHSV OF 1, AT ATMOSPHERIC PRESSURE, AND AT 2 MIN ONSTREAM TIMES

Catalyst	n-Butane converted to aromatics (wt %)	Ultimate recycle yield (wt %)	Butenes (wt %)	Coke (wt %)
Vanadia on eta-alumina	21	30	6	11.8
Vanadia on neutralized alumina	5	18	32.2	1.5
Vanadia on acidic alumina mixed with eta-alumina (2:1 vol ratio)	23	36	3.9	5.0
Vanadia on neutralized alumina mixed with eta-alumina (1:1 vol ratio)	27	39	2.7	4.7

concentration. Composition of the trimethylbenzenes is: 12% 1,2,3-trimethylbenzene, 66% 1,2,4-trimethylbenzene, and 22% 1,3,5-trimethylbenzene. Equilibrium values, calculated by Egan (*4*), were 10, 68, and 22%. Tri- and tetramethylbenzenes are formed from the xylenes via transmethylation catalyzed by the silica–alumina. The isobutylene/n-butenes ratio approaches equilibrium. About 1% pentenes and some cyclopentene and cyclopentadiene are also formed.

More coke is formed over mixtures with silica–alumina than with the other acid components. Inspection of a used chromia–alumina plus silica–alumina mixture shows that most of the coke is deposited on the silica–alumina. Increasing temperature, residence time, and catalyst onstream time further increase the rate of coke formation.

Oxides of Mn, Mo, V, and W

Dehydrocyclodimerization results over oxides of molybdenum, vanadium, tungsten,

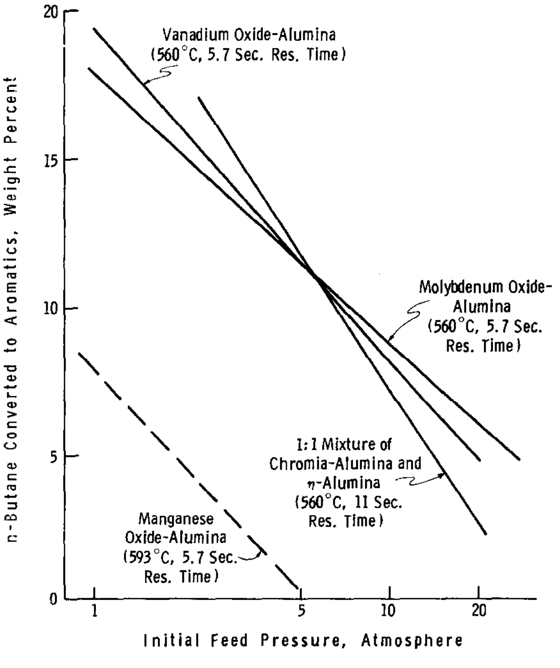


FIG. 7. Effects of pressure at constant residence time on n-butane conversions to aromatics.

TABLE 5
DEHYDROCYCLODIMERIZATION OF n-BUTANE WITH HELIUM DILUENT

Catalyst:	Mixture (1:1) of neutralized (0.2% K) vanadium oxide on alumina and eta-alumina		Mixture (1:1) of neutralized (0.1% K) chromia–alumina and eta-alumina		Molybdena on eta-alumina		
Initial n-butane partial pressure (atm):	0.43	1.0	0.43	1.0	0.43		1.0
Temp (°C):	560	593	560	593	560	560	560
LHSV:	0.21	0.48	0.21	0.48	0.82	0.41	0.95
Conversion to aromatics (wt %)	32	27	29	24	23	27	18
Ultimate recycle yield of aromatics (wt %)	49	40	44	40	41	28	32

and manganese on eta-alumina are summarized in Table 3. Yields are better (33 wt %) and conversions are higher (18.2 and 17.2 wt %) over the catalysts containing oxides of Mo and V. Conversions are lowest over the catalyst containing Mn. In mixtures, vanadia on a neutral support gives higher yields and conversions to aromatics than vanadia on acidic alumina because of lower coking (Table 4).

Conversions and yields decrease with increasing pressure with these catalysts (Figs. 7 and 8). The vanadium oxide–alumina catalyst performs better at all pressures than the other transition metal oxide catalysts.

Effect of Feed Diluents

Table 5 shows that conversions and yields are higher with helium than without a diluent over catalysts containing oxides of V, Cr, and Mo. The rate of aromatization increases with decreasing butane partial pressure. Table 6 presents results obtained with hydrogen diluent over various transition metal oxide catalysts. At a diluent/n-butane ratio of 1:1.27, yields and conversions to aromatics are significantly

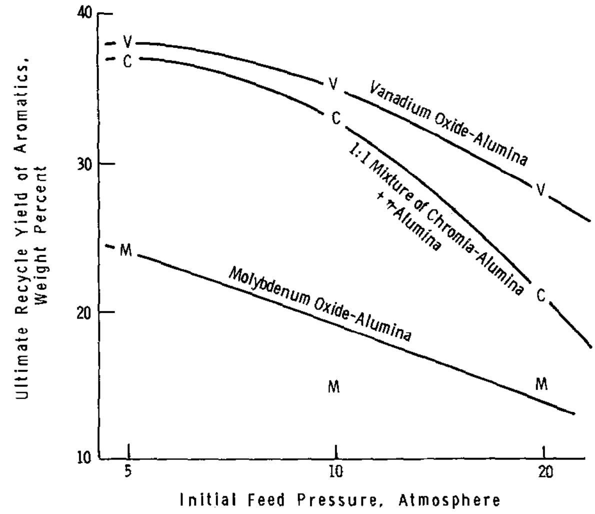


FIG. 8. Effect of pressure at a constant space velocity of 4.75 on ultimate recycle yields of aromatics at 560°C.

TABLE 6
DEHYDROCYCLODIMERIZATION OF *n*-BUTANE DILUTED WITH HYDROGEN OR HELIUM
(diluent/butane ratio = 1.27)

Catalyst:	Vanadium oxide (4% metal) on eta-alumina		Mixture of vanadium oxide (4% metal) on neutralized alumina and eta-alumina (1:1 vol ratio)			Mixture of chromia-alumina (0.1% K) and eta-alumina (1:1 vol ratio)		
Temp (°C):	593		560	593		560	593	
LHSV:	1.04		0.21	0.34		0.21	0.34	
Sampling time (min):	1	2	2	1	2	2	1	2
A. Hydrogen diluent (wt %)								
Unreacted butane	6.1	11.6	5.7	5.5	7.4	9.5	19.7	25.8
Butenes	2.8	3.7	2.5	1.6	3.5	4.0	5.7	7.6
C_1–C_2	44.1	38.6	38.4	41.1	36.0	30.7	25.0	20.9
Coke	5.4	6.0	3.6	2.0	4.4	5.7	2.1	2.4
Aromatics	18.8	16.0	24.7	24.6	21.7	21.9	17.5	15.1
Ultimate yield of aromatics	28	27	36	36	34	36	38	38
B. Helium diluent (wt %)								
Unreacted butane	6.9	22.5	10.2	2.3	4.9	10.4	24.3	18.5
Butenes	5.0	8.5	2.8	0.9	2.6	3.3	5.5	8.7
C_1–C_2	34.8	23.7	28.8	40.8	33.2	26.7	18.2	19.5
Coke	2.0	7.9	1.8	4.1	9.0	5.8	6.5	8.4
Aromatics	26.2	17.2	31.8	33.2	26.5	28.2	21.5	22.7
Ultimate yield of aromatics	40	34	49	41	37	44	44	42

lower with hydrogen than with helium because hydrogen depresses aromatization and increases hydrogenolysis.

CONCLUSIONS

Transition metal oxides might be preferred over Pt-containing dehydrocyclodimerization catalysts because they withstand better the frequent regeneration inherent in the process. We tested supported oxides of Cr, Mo, V, W, and Mn. The vanadium oxide–alumina catalyst performed best at all pressures.

REFERENCES

1. CSICSERY, S. M., *J. Catal.* **17**, 207 (1970).
2. CSICSERY, S. M., *J. Catal.* **17**, 216 (1970).
3. PINES, H., AND CHEN, C. T., *J. Amer. Chem. Soc.* **82**, 3562 (1960).
4. EGAN, C. J., *J. Chem. Eng. Data* **5**, 298 (1960).