

TABLE V. EFFECT OF *m*-TOLYLENE DIISOCYANATE IN VULCANIZING THIOKOL TYPE FA

| MTDI ^a | MBTS ^b | DPG ^c | Tensile Strength, Lb./Sq. In. | Ultimate Elongation, % | Hardness (Shore D) |
|-------------------|-------------------|------------------|-------------------------------|------------------------|--------------------|
| 5 | 0.3 | 0.1 | 425 | 370 | 65 |
| .. | 0.3 | 0.1 | 550 | 360 | 49 |
| 5 | .. | .. | 250 | 90 | 66 |
| .. | .. | .. | 150 | 270 | 51 |

Formulation. 100 parts polymer, 60 parts SRF black, 0.50 part stearic acid. Vulcanization time, 60 min. at 298° F.

^a *m*-Tolylene diisocyanate.

^b Benzothiazyl disulfide.

^c Diphenylguanidine.

TABLE VI. EFFECT OF PHENYL ISOCYANATE ON ZINC OXIDE VULCANIZATION OF THIOKOL TYPE FA

| Phenyl Isocyanate | MBTS ^a | DPG ^b | Tensile Strength, Lb./Sq. In. | Ultimate Elongation, % | Hardness (Shore D) |
|-------------------|-------------------|------------------|-------------------------------|------------------------|--------------------|
| 5 | 0.3 | 0.1 | 425 | 540 | 52 |
| 5 | .. | .. | 175 | 360 | 52 |

Formulation. 100 parts polymer, 60 parts SRF black, 0.5 part stearic acid, 10 parts zinc oxide.

Vulcanization time, 60 min. at 298° F.

^a Benzothiazyl disulfide.

^b Diphenylguanidine.

then treated with dithiodiglycol to effect disulfide redistribution (1) and produce a polymer with hydroxyl terminals. The treated polymer had a Williams plasticity of 116. The results of compounding, curing, and testing of the three polymers are presented in Table VII. It is seen that the physical properties are equivalent for all three materials.

All evidence, therefore, points to the presence of hydroxyl terminals in the Type FA polymer. Chlorine terminals would be

TABLE VII. EFFECT OF INTRODUCTION OF HYDROXYL TERMINALS ON THIOKOL TYPE FA

| Treatment | Plasticity (Williams) | Tensile Strength, Lb./Sq. In. | Modulus 300%, Lb./Sq. In. | Elongation, % | Hardness (Shore D) |
|-------------------|-----------------------|-------------------------------|---------------------------|---------------|--------------------|
| FA control | 125 | 1200 | 950 | 470 | 71 |
| FA, toughened | 299 | 1275 | 1150 | 380 | 73 |
| Hydroxy terminals | 116 | 1150 | 875 | 430 | 68 |

Formulation. 100 parts polymer, 60 parts SRF black, 10 parts zinc oxide, 0.5 part stearic acid, 0.3 part benzothiazyl disulfide, 0.1 part diphenylguanidine.

Vulcanization time, 30 min. at 298° F.

expected to react with zinc oxide, but not with diisocyanates. The lack of success with organic oxidizing agents eliminates thiol terminals. There is no indication that olefin terminals possess the required reactivity to zinc oxide. Although the action of zinc oxide in causing end-to-end coupling of the polymer chains is not understood, the fact that polymers in which hydroxyl terminals are deliberately introduced are vulcanized by zinc oxide is strong evidence of hydroxyl terminals in Thiokol Type FA.

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Improved Butane Dehydrogenation Catalysts

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THE increasing use of butenes and butadiene by the petroleum, chemical, and plastics industries emphasizes the importance of butane dehydrogenation catalysts to these industries. These dehydrogenation catalysts play a major role in determining the design and capacity of butane dehydrogenation plants, the efficiency of their operation, and ultimately, the economics of finished products made from butenes and butadiene.

Several compositions and methods of preparing catalysts for the dehydrogenation of *n*-butane have been investigated and have been summarized by Howard (12). The better known of these catalysts are composed of chromia (13), chromia-alumina (10, 11, 18), or chromia-alumina modified with an alkali (2, 5, 22), zinc compounds (2, 22), or beryllia (17, 19). These catalysts are prepared by impregnating hydrated or activated alumina (5, 10, 11, 18), precipitation (13, 17, 19), mixing gels (4), and mixing gels with other materials (2, 22). The use of such catalysts in laboratory, pilot plant, and full scale plant studies is described by Frey and Huppke (3), Grosse and Ipatieff (6), Hachmuth and Hanson (7), Hanson and Hays (8), Howard (12), and Lassiat (15).

The aim of the present work was to find a catalyst that is more active than present standard catalysts. The work includes an investigation of the effect on catalyst activity of various new or

modified methods of preparing catalysts and of catalyst composition. Among the most promising methods of preparing catalysts investigated were digestion in ammonium nitrate and digestion in nitric acid. Less effective methods were: thermal decomposition of metal compounds, impregnation of activated alumina pills, impregnation of gel alumina pills, and combinations of these. The effect of chromia, beryllia, and potassa on the activity of catalysts prepared by the digestion techniques was also studied.

CATALYST PREPARATIONS

AMMONIUM NITRATE DIGESTION METHOD. Hydrated alumina (Aluminum Co. of America, Grade C-31) and reagent grade chromium trioxide were mixed with a trace of water and an amount of reagent grade ammonium nitrate equal to three times the weight of the finished catalyst. The mixture was digested in a 1-liter round-bottomed flask with stirring at 149° to 163° C. (300° to 325° F.) under total reflux for 44 hours. Ammonium nitrate was removed from the digested material by heating it to 463° C. (865° F.) in about 2 hours and maintaining it at that temperature for 5 hours. This material was cooled to room temperature, ground to pass a 50-mesh sieve, mixed with an amount of pilling lubricant equal to 5% of the finished catalyst, and

formed into pills $\frac{1}{8}$ inch in length and diameter. Lubricant was removed from the pills by heating them in air at a space velocity of about 700 to a temperature of 538° C. (1000° F.) in 3 hours and maintaining them at that temperature for 20 hours (20). Special safety precautions must be taken in using ammonium nitrate (14, 23).

NITRIC ACID DIGESTION METHOD. Hydrated alumina (Aluminum Co. of America, Grade C-31) and reagent grade chromia (Cr_2O_3) were mixed with an amount of 70% reagent grade nitric acid equivalent to three times the weight of the finished catalyst. This mixture was digested in a 1-liter round-bottomed flask by stirring and boiling it under total reflux for 44 hours. Nitric acid was removed from the digested material by heating it to 416° C. (780° F.) in 30 minutes and maintaining it at that temperature for 15 hours. This material was cooled to room temperature, ground to pass a 100-mesh sieve, mixed with an amount of pilling lubricant and water equal to 5 and 10%, respectively, of the weight of the finished catalyst, and formed into pills $\frac{1}{8}$ inch in length and diameter. Lubricant was removed from the pills by heating them in air at a space velocity of about 770 to a temperature of 538° C. (1000° F.) in 3 hours and maintaining them at that temperature for 20 hours (20, 21). When this catalyst is prepared to contain beryllia, extensive safety precautions must be taken in preparing or testing it (1, 9, 16, 24).

IMPREGNATION METHOD (Standard Reference Catalyst). Hydrated alumina (Aluminum Co. of America, Grade C-31) was heated at about 350° C. (662° F.) for 3 hours, cooled to room temperature, mixed with an amount of pilling lubricant equivalent to 5% of the heated alumina, and formed into pills $\frac{1}{8}$ inch in length and diameter. Lubricant was partially removed from the pills by heating them in air to about 538° C. (1000° F.) and rapidly cooling them to room temperature (18). These pills were immersed in an aqueous solution of chromic acid, drained, dried, and calcined at 538° C. (1000° F.) to give a catalyst containing 20% chromia and 80% alumina.

CATALYST TESTING

CYCLING PROCEDURE. Portions of each catalyst (10 cc.) were tested in alternate 1-hour dehydrogenation and catalyst regeneration periods. During the dehydrogenation period, *n*-butane at atmospheric pressure was passed over the catalyst at a temperature in the range of 566° C. (1050° F.) and an *n*-butane space velocity of about 700 to 750. After the 1-hour dehydrogenation period, the catalyst was regenerated at atmospheric pressure by passing air over it at a space velocity of about 800 and a temperature in the range of 580° C. (1076° F.). The temperature during the regeneration period usually reached a peak of about 605° C. (1121° F.). All temperatures were determined at the mid-point of the catalyst bed. Following the regeneration period, the catalyst was again used for dehydrogenation.

CYCLING EQUIPMENT. The equipment for cycling catalysts consisted of a battery of 12-inch electrical tube furnaces equipped with automatic temperature controllers; borosilicate glass catalyst tubes, 17 mm. in outside diameter, constructed to support a 10-cc. portion of catalyst equidistant from the ends of the 12-inch furnace and equipped with a coaxial thermocouple well extending to the bottom of the catalyst bed; and laboratory gas flowmeters. The switching between dehydrogenation and regeneration periods was automatically controlled by an apparatus consisting of a mercury cutoff valve system operated by an electrical-mechanical control system which raised and lowered mercury reservoirs.

ANALYTICAL PROCEDURE. The total product from a 1-hour dehydrogenation period was collected in the low-temperature distillation apparatus, the product was separated into H_2 to CH_4 , C_2 , C_3 , C_4 , and C_{5+} fractions; the H_2 in the H_2 to CH_4 fraction was determined either with the mass spectrometer or by copper oxide combustion; olefins in the C_2 and C_3 fractions were determined by absorption in sulfuric acid; olefins in the C_4 fraction were determined by absorption of the monoolefins in sulfuric acid and butadiene in maleic anhydride, by infrared analysis, or by absorption of all olefins in mercuric nitrate solution; isobutylene was determined by absorption in sulfuric acid; the amount of the C_{5+} fraction was determined by weighing the residue in the fractionating-column kettle; and the coke deposited on the catalyst was determined by absorbing the water and car-

bon dioxide formed during the catalyst regeneration period in magnesium perchlorate and potassium hydroxide, respectively.

MATERIALS FOR TESTING. *n*-Butane varying from 96.3 to 99.4% in purity (the principal impurity was isobutane), and compressed air which contained about 0.002 gram of water per liter, were used.

TERMINOLOGY

In this paper conversion is defined as the per cent of *n*-butane destroyed in a single pass, selectivity or efficiency is the per cent of destroyed butane that is converted to *n*-butenes plus butadiene, yield is the per cent of the *n*-butane that is converted to *n*-butenes plus butadiene in a single pass, per cent is weight per cent, space velocity is gaseous volumes (0° C., 760 mm.) per bulk catalyst volume per hour, and potassa is potassium hydroxide.

DISCUSSION

In an investigation of this nature, the need for a simplified method of rating catalysts is immediately evident. Other investigators have introduced a method of rating which consists of analyzing the product from a dehydrogenation experiment, determining the experimental conversion and selectivity from the data, and adding these two figures. This rating has no direct physical significance itself, and, in order to overcome this difficulty, a modification of this method has been introduced.

The modified method consists of calculating the yield at a selectivity of 80% from experimental data. This method is based on the assumption that for a particular catalyst at a specific age the sum of the conversion and selectivity is constant over the relatively narrow range of variations from 80% selectivity which was experimentally obtained in this work. Such an assumption is supported by data in Table I, which were taken from temperature-conversion studies made at a constant catalyst age by varying the temperature while all other experimental conditions remained essentially constant.

TABLE I. COMPARISON OF YIELD CALCULATED AT 80% SELECTIVITY

| | Experimental Results | | | Yield at 80% Selectivity | |
|--|----------------------|-------------|--------------------------|--------------------------|------------------------|
| | Conversion | Selectivity | Conversion + selectivity | Calculated yield | Deviation from average |
| Nitric acid-digested catalyst (45-day age) | 51.3 | 74.9 | 126.2 | 37.0 | +0.4 |
| | 37.8 | 86.7 | 124.5 | 35.6 | -1.0 |
| | 46.2 | 80.4 | 126.6 | 37.3 | +0.7 |
| Standard reference catalyst (1-day age) | 53.8 | 66.5 | 120.3 | 32.2 | -0.9 |
| | 50.1 | 72.0 | 122.1 | 33.7 | +0.6 |
| | 46.1 | 76.0 | 122.1 | 33.7 | +0.6 |
| | 40.3 | 80.4 | 120.7 | 32.6 | -0.5 |

The yields at 80% selectivity shown in Table I were calculated from the experimental data by adding the experimental conversion and selectivity, subtracting 80 from the sum, and multiplying the difference by 0.8. The precision of the yield at 80% selectivity is illustrated by the deviation from the average yield and is not greater than 1.0 percentage point.

Although this method of rating catalysts has not been thoroughly established, it is used in the following discussion. Only the more important variables in the preparation of both ammonium nitrate-digested and nitric acid-digested catalysts are discussed in this paper and the yields for the best catalysts prepared by these methods are compared with the yield for a standard reference catalyst.

AMMONIUM NITRATE DIGESTION METHOD. The procedure presented above was used to prepare chromia-alumina catalysts which contained 20, 40, and 60% chromia and 0.0, 0.75, 1.50, and 3.0% potassa, and were digested for 1, 8, 32, and 44 hours. The

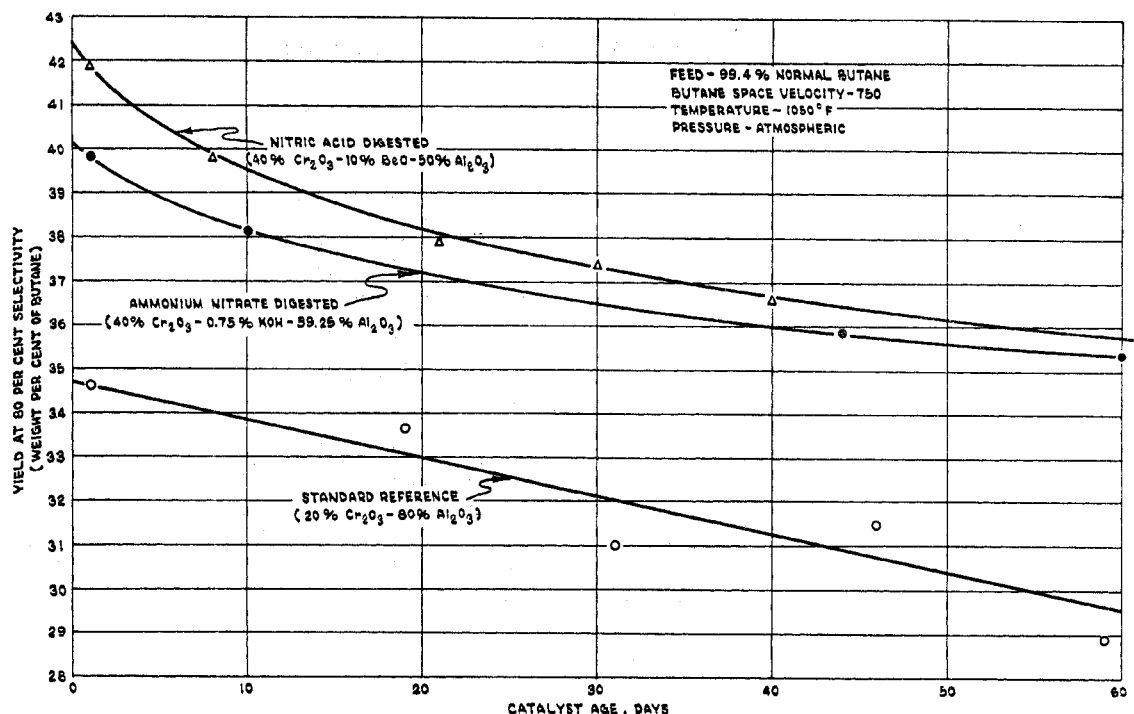


Figure 1. Yield of *n*-Butenes Plus Butadiene

For catalysts prepared by ammonium nitrate digestion, nitric acid digestion, and impregnation (standard reference catalyst)

potassa was added to the catalyst before the digestion period in the form of potassium dichromate.

Table II shows that 20, 40, and 60% chromia catalysts have similar yields at an age of 1 day; at an age of 20 days, the 60% chromia catalyst is definitely less active than the others. Data for longer periods of operation for the 20 and 40% chromia catalysts, not shown in the table, indicate that the 40% chromia may be better.

The yields for catalysts which contain potassa (Table II) show that 0.75% may be desirable; however, larger amounts are objectionable.

The yields for a 40% chromia-0.75% potassa-59.25% alumina catalyst which was digested for periods varying from 1 to 44 hours (Table II) show that the length of the digestion period is not critical between 1 and 44 hours.

Based on this study, a catalyst which contained 40% chromia, 0.75% potassa, and 59.25% alumina and had been digested in ammonium nitrate for 44 hours was selected for a 60-day life test.

TABLE II. YIELDS^a FOR AMMONIUM NITRATE-DIGESTED CATALYSTS

| Catalyst | Cr ₂ O ₃ , % | Catalyst Age, Days | |
|---|------------------------------------|--------------------|-------------------|
| | | 1 | 20 |
| 0.75% KOH, balance Cr ₂ O ₃ and Al ₂ O ₃ , 44-hr. digestion | 20 | 41.4 | 37.6 |
| | 40 | 39.8 | 37.2 ^b |
| | 60 | 40.6 | 29.7 |
| 40% Cr ₂ O ₃ , balance Al ₂ O ₃ and KOH, 44-hr. digestion | KOH, % | 0 | 38.6 |
| | | 0.75 | 39.8 |
| | | 1.50 | 38.6 |
| | | 3.00 | 27.7 |
| 40% Cr ₂ O ₃ , 0.75% KOH, balance Al ₂ O ₃ | Digestion, Hours | 1 | 39.4 |
| | | 8 | 38.9 |
| | | 32 | 41.1 |
| | | 44 | 39.8 |

^a At selectivity of 80%.

^b Value taken from Fig. 1.

TABLE III. YIELDS^a FOR NITRIC ACID-DIGESTED CATALYSTS

| Catalyst | Cr ₂ O ₃ , % | Catalyst Age, Days | |
|--|------------------------------------|--------------------|-----------------|
| | | 1 | 20 ^b |
| Balance Al ₂ O ₃ , 44-hr. digestion | 20 | 21.0 | .. |
| | 40 | 35.1 | 30.9 |
| | 60 | 38.3 | 33.0 |
| 40% Cr ₂ O ₃ , balance BeO and Al ₂ O ₃ , 44-hr. digestion | BeO, % | 0.0 | 35.1 |
| | | 2.5 | 40.0 |
| | | 5.0 | 41.8 |
| | | 10.0 | 41.8 |
| 40% Cr ₂ O ₃ , 10% BeO, 50% Al ₂ O ₃ | Digestion Period, Hours | 0 | 31.5 |
| | | 2 | 34.6 |
| | | 12 | 38.7 |
| | | 44 | 41.8 |
| | | 192 | 39.4 |
| | | .. | .. |

^a At selectivity of 80%.

^b When selected catalysts were tested at 20-day age, no changes in 1-day relationships were observed. Because of this, other catalysts were not tested at 20 days and conclusions are based on 1-day tests.

NITRIC ACID DIGESTION METHOD. The procedure presented above was used to prepare chromia-alumina catalysts which contained 20, 40, and 60% chromia and 0, 2.5, 5.0, and 10.0% beryllia, and were digested for 0, 2, 12, 44, and 192 hours. When beryllia was made a part of the catalyst, pure grade beryllia was added to the mixture before it was digested.

Table III shows that the yield increases as the chromia content of the catalyst is increased to 60%. This relationship between chromia content and yield is different from that for the ammonium nitrate-digested catalyst (Table II), where different chromia contents do not change the yield.

The yields for catalysts that contain beryllia (Table III) show that about 5% beryllia is optimum, and all catalysts that contain beryllia give higher yields and have longer lives than catalysts without beryllia.

TABLE IV. LABORATORY DATA FOR BUTANE DEHYDROGENATION

| Catalyst Age, Days ^a | Butane Space Velocity ^b | Average Temp., ° F. ^c | % Butane Converted ^d | Yield, Single-Pass ^d | Selectivity ^d | Yield, Single-Pass Calcd. at 80% Selectivity | Product Analysis | | | | | | | | | |
|---|------------------------------------|----------------------------------|---------------------------------|---------------------------------|--------------------------|--|------------------|-----------------|----------------|----------------|----------------------------------|---|--------------------------------|-----------------------------|------------------|--|
| | | | | | | | H ₂ | CH ₄ | C ₂ | C ₃ | i-C ₄ H ₁₀ | C ₄ H ₆ ⁺ n-C ₄ H ₈ | C ₄ H ₁₀ | C ₃ ⁺ | Coke on catalyst | |
| Ammonium Nitrate-Digested Catalyst (40% Cr ₂ O ₃ -0.75% KOH-59.25% Al ₂ O ₃) | | | | | | | | | | | | | | | | |
| 1 | 753 | 1052 | 47.8 | 39.2 | 82.0 | 39.8 | 1.91 | 0.71 | 1.61 | 1.56 | 0.90 | 39.02 | 51.86 | 1.07 | 1.36 | |
| 10 | 749 | 1052 | 44.8 | 37.1 | 82.8 | 38.1 | 1.76 | 0.61 | 1.38 | 1.39 | 0.91 | 36.91 | 54.90 | 0.94 | 1.20 | |
| 44 | 752 | 1055 | 41.2 | 34.5 | 83.7 | 35.9 | 1.60 | 0.51 | 1.55 | 1.13 | 0.92 | 34.29 | 58.44 | 0.69 | 0.87 | |
| 59 | 752 | 1058 | 40.4 | 33.8 | 83.7 | 35.3 | 1.60 | 0.51 | 1.26 | 1.27 | 0.92 | 33.63 | 59.21 | 0.84 | 0.76 | |
| Nitric Acid-Digested Catalyst (40% Cr ₂ O ₃ -10% BeO-50% Al ₂ O ₃) | | | | | | | | | | | | | | | | |
| 1 | 746 | 1059 | 53.5 | 42.2 | 78.9 | 41.9 | 2.17 | 1.29 | 2.24 | 2.23 | 0.87 | 41.49 | 46.21 | 0.75 | 2.36 | |
| 8 | 761 | 1047 | 46.0 | 38.5 | 83.7 | 39.8 | 1.82 | 0.60 | 1.62 | 1.13 | 0.91 | 38.31 | 53.65 | 0.87 | 1.09 | |
| 21 | 750 | 1049 | 43.8 | 36.6 | 83.6 | 37.9 | 1.69 | 0.60 | 1.24 | 1.65 | 0.91 | 36.37 | 55.91 | 0.73 | 0.90 | |
| 30 | 755 | 1048 | 42.7 | 35.9 | 84.1 | 37.4 | 1.66 | 0.50 | 1.41 | 0.95 | 0.92 | 35.73 | 57.04 | 0.83 | 0.96 | |
| 61 | 746 | 1052 | 39.5 | 33.6 | 85.1 | 35.7 | 1.50 | 0.54 | 1.20 | 0.91 | 0.93 | 33.39 | 60.05 | 0.77 | 0.71 | |
| Impregnated Reference Catalyst (20% Cr ₂ O ₃ -80% Al ₂ O ₃) | | | | | | | | | | | | | | | | |
| 1 | 757 | 1050 | 42.0 | 34.1 | 81.2 | 34.6 | 1.67 | 0.82 | 1.59 | 1.03 | 0.91 | 33.87 | 57.66 | 0.94 | 1.51 | |
| 19 | 727 | 1049 | 41.4 | 33.4 | 80.7 | 33.7 | 1.47 | 0.84 | 1.67 | 1.48 | 0.90 | 33.20 | 58.20 | 1.05 | 1.19 | |
| 31 | 723 | 1051 | 37.3 | 30.4 | 81.5 | 31.0 | 1.44 | 0.63 | 1.65 | 1.29 | 0.92 | 30.24 | 62.27 | 0.65 | 0.91 | |
| 46 | 740 | 1055 | 37.7 | 30.8 | 81.7 | 31.5 | 1.40 | 0.72 | 1.58 | 1.53 | 0.91 | 30.56 | 61.87 | 0.66 | 0.77 | |
| 59 | 753 | 1054 | 35.0 | 28.4 | 81.1 | 28.9 | 1.28 | 0.58 | 1.40 | 1.70 | 0.92 | 28.23 | 64.56 | 0.70 | 0.63 | |

^a Catalyst age includes both dehydrogenation and catalyst regeneration periods.
^b Gaseous volumes (0° C., 760 mm.) per bulk volume of catalyst per hour.
^c Temperature during dehydrogenation period. Temperature during catalyst regeneration period usually reached a peak of 1121° F. and averaged about 1076° F.
^d Equations. % butane converted = (butane in feed - butane in product)/butane in feed.
 Yield, single-pass = (n-butenes + butadiene in product)/butane in feed.
 Selectivity = yield, single-pass/% butane converted.

General Conditions.
 Pressure, Atmospheric
 Feed, 99.4% n-butane (principal impurity isobutane)
 All percentages are by weight

For catalysts digested for periods varying from 0 to 192 hours (Table III), the yield increases as the digestion period is lengthened up to at least 12 hours, and may be optimum around 44 hours.

Based on this study, a catalyst which contained 40% chromia, 10% beryllia, and 50% alumina and had been digested in nitric acid for 44 hours was selected for a 60-day life test.

EXTENDED LIFE TESTS ON CATALYSTS. Catalysts selected for life tests from the series of ammonium nitrate- and nitric acid-digested catalysts were tested continuously for 60 days and yields were determined at various times during the tests. As a control the standard reference catalyst was also tested. Yields at 80% selectivity were calculated from the experimental results presented in Table IV and are shown in Figure 1. Yields taken from the curves of Figure 1 at catalyst ages of 1 and 60 days are presented in Table V.

These data show that the yields from both of the digested catalysts are greater than the yield from the standard reference catalyst by 15.0 to 21.0%, that the drop in yield during the 60-day test was less for the digested catalysts than for the standard catalyst, and that the nitric acid-digested catalyst, which contains beryllia, gave a higher yield throughout the 60-day period than the ammonium nitrate-digested catalyst.

CONCLUSIONS

Chromia-alumina butane dehydrogenation catalysts prepared by ammonium nitrate digestion (40% Cr₂O₃-60% Al₂O₃) and nitric acid digestion (40% Cr₂O₃-10% BeO-50% Al₂O₃) are superior to an impregnated standard catalyst (20% Cr₂O₃-80% Al₂O₃). These superior catalysts give 15 to 21% higher yields at a selectivity of 80% than are realized from the standard catalyst.

TABLE V. SUMMARY OF DATA ON LIFE TESTS

| | Catalyst Age, Days | | | | % Drop in Yield from 1 to 60 Days |
|----------------------------|--------------------|-------------------------|-------|-------------------------|-----------------------------------|
| | 1 | | 60 | | |
| | Yield | % greater than standard | Yield | % greater than standard | |
| Ammonium nitrate digestion | 39.8 | 15.0 | 35.2 | 19.3 | 11.6 |
| Nitric acid digestion | 41.9 | 17.4 | 35.7 | 21.0 | 14.8 |
| Impregnation-standard | 34.6 | 0.0 | 29.5 | 0.0 | 15.5 |

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