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Isomerization of *n*-Butene to Isobutene*

I. Selection of Catalyst by Group Screening

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The group screening method has been applied to the selection of the best catalyst for the isomerization of *n*-butene to isobutene, as the first step in a detailed program of investigations on the mechanism and kinetics of this reaction. Forty-six acid-solid catalysts grouped according to their chemical similarities into twelve groups have been tested for their performance in the conversion of *n*-butene to isobutene at 400°C, atmospheric pressure and $W/F = 40$ [ratio of the catalyst weight (g) to the feed rate (gmole/hr)] in an integral-type reactor. Constituent catalysts of the group which appeared to contain the most promising catalysts were then tested independently under identical conditions in order to identify the best catalyst. Fluorinated η-alumina (1% F) was found to be the best catalyst, with the highest activity (conversion), good selectivity, appropriate life, and excellent regenerability. It was possible to identify the best catalyst in only 17 runs by the group screening method as against a minimum of 46 that would have been necessary if all the catalysts had been assessed independently (excluding life and regeneration tests in both cases).

INTRODUCTION

The selection of the best catalyst for a particular catalytic reaction is one of the most important problems in catalyst research and screening. Since a large variety of catalysts are available, it is often rather an expensive and time consuming process to select the best catalyst by conventional experimental procedures, i.e., by testing each catalyst individually.

Recently, Hunter and Mezaki (*3*) have indicated a method to overcome this difficulty by employing the so-called "group screening" technique (*1*) to catalyst selection for methane oxidation. Fourteen commercially available catalysts were tested in only seven runs by grouping all the catalysts into seven groups. According to Watson (*4*), "group screening methods are those procedures which involve the idea of putting the factors in groups, testing these group factors, and then testing the factors in the significant group factors."

In the group screening method as applied to the rapid selection of the best catalyst for a given reaction, the catalysts are tested for their response in groups, i.e., instead of a single catalyst being charged to the reactor, a mixture of a number of catalysts (those having close chemical similarities) in equal parts by weight, is used and the test is carried out. After all these groups are tested, the constituent catalysts of those groups which appear to contain promising catalysts are tested in order to select the best individual catalysts. It is assumed in the group screening technique that (i) the catalysts in a group do not interact, and (ii) the presence of any catalyst "adds to, but never subtracts from, the conversion." The success of this method is mainly based on the above two assumptions. The physicochemical nature of the catalyst (*2*) is such that there is no reason to doubt the validity

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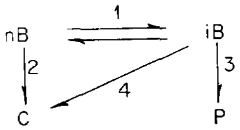
of the first assumption but the second assumption is not always valid, particularly when complex-consecutive reactions are involved and our interest lies in an intermediate product. If, however, we are concerned with the overall conversion of the reactant, the group screening method would still be applicable.

Let us take the present reaction, which can be represented as



where *n*B, *i*B, *C*, and *P* denote respectively normal butene, isobutene, cracking products, and polymerization products. Preliminary experimental studies carried out as part of the present work, with *n*B and *i*B as starting materials, have clearly shown that polymerization products are not formed from *n*-butene. The application of the group screening method to this reaction would not be justified in the normal course since we are interested in the intermediate product *i*B and it is possible that one catalyst of the group would promote Step (1) while another only Step (3). In such a case, the conversion to *i*B obtained with the first catalyst would be reduced by the second catalyst which tends to eliminate *i*B, thus introducing a negative effect. Since, fortunately, the formation of *P* is negligible, all the effects can be assumed to be non-negative, which is the basis of the group screening method. Further, at the temperature, pressure and *W*/*F* employed, the formation of *C* is also negligible.

It should be noted that hypothetically the "best" catalyst having all the desirable properties, such as highest activity, selectivity and stability (life), lowest ignition (or activation or calcination) temperature and cost, and ease of regeneration, may not exist (and generally does not exist). For example, one catalyst may possess the highest activity but a low selectivity and stability compared to another catalyst or vice-versa, and hence one has to be careful while choosing the principal response for catalyst selection by group screening. In cases where reactants are costly, the catalyst with the highest selectivity is desirable, while in cases where reactants are cheaper as compared to products the highest activity is preferred. Apart from the principal responses (activity and/or selectivity), auxiliary responses such as stability (or life), ease of regeneration, and catalyst cost should also be considered while selecting a catalyst for a particular catalytic process.

The aim of the present study was to employ the group screening method for the selection of the best catalyst for the catalytic isomerization of *n*-butene to isobutene. Forty-six acid-solid catalysts were tested essentially in 17 runs by considering activity and selectivity as the principal responses and life and ease of regeneration as auxiliary responses. Results of detailed kinetic analysis using the "best" catalyst thus selected will be communicated in a subsequent paper.

EXPERIMENTAL

Reaction System Studied

The skeletal isomerization of *n*-butene to isobutene takes place by passing *n*-butene at atmospheric pressure over an acidic solid catalyst heated at about 400°C.

$$n\text{-Butene} \underset{400^\circ\text{C}}{\overset{\text{acid catalyst}}{\rightleftharpoons}} \text{Isobutene}$$

which is a simplified version of the scheme presented earlier, and is valid under the conditions employed. As already mentioned, apart from the isobutene and unconverted *n*-butene, the gaseous product contains in some cases a little amount of liquid polymer and hydrocarbons containing less than four carbon atoms formed by cracking. The analysis of the liquid polymer by ir, NMR, and mass spectroscopy showed that is a branched chain structure similar to the structure of polyisobutene.

Starting Materials

***n*-Butene.** *n*-Butene (99.5%) was prepared by the catalytic dehydration of

TABLE 1

CATALYSTS USED, THEIR GROUPING AND PREPARATION

Group	Catalyst			Calcination temp (°C)
	No.	Type	Preparation	
I	1	Bauxite	Natural Indian bauxite	400
	2	Fluorinated bauxite (0.5% F)	Impregnating activated bauxite (Catalyst 1) with ammonium fluoride from solution containing appropriate amounts of fluorine and drying at 110°C for 10 hr	450
	3	Fluorinated bauxite (1.0% F)		450
	4	Fluorinated bauxite (1.5% F)		450
	5	Fluorinated bauxite (2.0% F)		450
II	6	Boron orthophosphate	Heating boric acid (12.4 g) and phosphoric acid (24 g) at 200°C and crushing of resulting cake to required size	500
	7	Boron orthophosphate activated by 3% Cr	Similar to Catalyst 6 with chromium oxide added to the reaction mixture	500
	8	Boron orthophosphate activated by Fe, Mn, and Cr	Similar to Catalyst 6 with ferric oxide, manganese dioxide, and chromium oxide added to the reaction mixture	500
	9	Phosphoric acid on silica gel	Soaking silica gel in phosphoric acid and drying at 110°C	400
	10	Phosphoric acid on alumina	Soaking alumina in phosphoric acid and drying at 110°C	400
III	11	Silica–alumina	Davidson grade	450
	12	Fluorinated silica–alumina (0.5% F)	Impregnating silica–alumina (Catalyst 11) with ammonium fluoride from solution containing appropriate amount of fluorine and drying at 110°C for 10 hr	450
	13	Fluorinated silica–alumina (1.0% F)		450
	14	Fluorinated silica–alumina (1.5% F)		450
	15	Fluorinated silica–alumina (2.0% F)		450
IV	16	η-alumina (acidic)	Precipitating aluminium trihydroxide (β-trihydrate) from aluminium nitrate solution by ammonium hydroxide at 8.2–8.5 pH at room temp, washing, filtering and drying the precipitate at 110°C for 72 hr, and then igniting in air at 650°C	650
	17	Fluorinated η-alumina (0.5% F)	Impregnating η-alumina (Catalyst 16) with ammonium fluoride from solution containing appropriate amount of fluorine and drying at 110°C for 10 hr	450
	18	Fluorinated η-alumina (1% F)		450
	19	Fluorinated η-alumina (1.5% F)		450
	20	Fluorinated η-alumina (2% F)		450
V	21	Chromia–silica (5% Cr_2O_3)	Impregnating silica gel with ammonium dichromate from solution containing appropriate amount of Cr_2O_3 and drying at 110°C for 10 hr	450
	22	Chromia–silica (10% Cr_2O_3)		450
	23	Chromia–alumina (5% Cr_2O_3)	Impregnating η-alumina (Catalyst 16) with ammonium dichromate from solution and drying at 110°C for 10 hr	450
	24	Chromia–alumina (10% Cr_2O_3)		450

TABLE 1 (*Continued*)

Group	Catalyst			Calcination temp (°C)
	No.	Type	Preparation	
VI	25	Molybdena-silica (5% MoO_3)	Impregnating silica gel or η-alumina (Catalyst 16) with ammonium molybdate from solution of appropriate strength	450
	26	Molybdena-silica (10% MoO_3)		450
	27	Molybdena-alumina (5% MoO_3)		450
	28	Molybdena-alumina (10% MoO_3)		450
VII	29	Pt-alumina (0.5% Pt)	Impregnating η-alumina or silica-alumina with platinum or palladium chloride from solution of appropriate strength	400
	30	Pd-alumina (0.5% Pd)		400
VIII	31	Pt-silica-alumina (0.5% pt)		400
	32	Pd-silica-alumina (0.5% pd)		400
IX	33	Magnesia-alumina (10% MgO)	Coprecipitating aluminium hydroxide and magnesium hydroxide from solution containing aluminium nitrate and magnesium sulphate by ammonium hydroxide at room temperature, washing the resulting precipitate, filtering and drying it at 110°C for 48 hr	450
	34	Magnesia-alumina (20% MgO)		450
	35	Ferric oxide-alumina (1% Fe_2O_3)	Coprecipitating ferric hydroxide and aluminium hydroxide from solution containing ferric chloride and aluminium nitrate by ammonium hydroxide at room temperature, washing the resulting precipirate, filtering and drying at 110°C for 48 hr	450
	36	Ferric oxide-alumina (2% Fe_2O_3)		450
X	37	Zinc chloride (with $FeCl_3$, $AlCl_3$ and $MgCl_2$) on η-alumina (25% $ZnCl_2$)	Impregnating η-alumina with metal chloride from solution containing appropriate amount of metal chloride and promoters	450
	38	Lanthanum and cerium chloride on alumina (20% $LaCl_3$ and $CeCl_3$)		450
	39	Chlorinated alumina (3.5% Cl)	Impregnating η-alumina with ammonium chloride from solution of appropriate strength	450
XI	40	H-faujasite	Base exchange of Na^+ from Na-faujasite with NH_4^+ from ammonium chloride solution washing and drying at 110°C	500
	41	Fluorinated faujasite (1% F)	Impregnating H-faujasite (Catalyst 40) with ammonium fluoride from solution	450
	42	Fluorinated faujasite (2% F)		450
XII	43	Pt-faujasite (0.5% pt)	Impregnating H-faujasite (Catalyst 40) with Pt or Pd chloride from solution	450
	44	Pd-faujasite (0.5% pd)		450
	45	La-faujasite	Base exchange of Na^+ from Na-faujasite with La^{3+} or Ce^{3+} from their chloride solutions.	450
	46	Ce-faujasite		450

n-butanol on basic alumina (Alcoa dehydration grade) at 330–350°C with a space velocity of 0.475 moles/ml/hr in a fixed-bed reactor which gave a conversion of 92% with 96 to 98% selectivity. The product gases (containing 98.5–99% n-butene) were collected in a gas holder and compressed in a cylinder where they liquified. The cylinder was then kept in an ice-bath at 0°C, and the pressure in the cylinder (which was mostly due to the lower boiling gases) was released to atmosphere. This procedure was repeated till the analysis of the out coming gas reached 99.5% n-butene.

Isobutene. Isobutene (purity 99.5%) was prepared by the catalytic dehydration of tertiary butanol by H-cation exchange resin (NCL grade) by refluxing t-butanol (250 ml) under stirring with H-cation exchange resin (2.0 g) in a three-necked flask fitted with a glass stirrer and reflux condenser.

Catalysts. All the forty-six catalysts used, except silica gel and silica–alumina, were prepared in the laboratory. Procedures for the preparation of these catalysts are described briefly in Table (1).

Reactor System

The reactor used for carrying out activity tests was an integral-type reactor made of mild-steel and heated with a fluidizing bed of solids (bauxite) to maintain isothermal conditions. A capillary flow meter was used to measure gas-flow rates and a water condenser to condense liquid products. A gas collector with mercury seal and water displacement arrangement was used for gas collection.

Analysis of Products

The liquid product (polyisobutene) was determined directly by weighing, while the gaseous product was analysed for isobutene and n-butene by selective absorption in 60.5 wt/wt % and 90 wt % H_2SO_4 (AR), respectively, in an Orsat apparatus. The method of analysis of n-butene and isobutene was standardized by carrying out the analysis of pure n-butene, isobutene, and of mixtures of n-butene and isobutene of known composition. The products due to cracking were determined from material balance.

RESULTS AND DISCUSSION

The forty-six catalysts used were divided into twelve groups according to their chemical similarities, each group containing two to five individual catalysts (Table 1). The catalyst for any particular group was prepared by adding equal quantities of the constituent members. The activity runs were then carried out at 400°C and $W/F = 40$. After testing all the 12 groups, the constituent catalysts of the group which gave the best results were tested under identical experimental conditions in order to select the best individual catalyst.

Life tests on the promising catalysts were carried out in the same reactor under the experimental conditions used for group and subgroup testing till the activity of the catalyst reduced to half its initial activity. The regeneration of a catalyst (deactivated during life test) was carried out by igniting it in the presence of air at 500°C followed by activity tests.

The experimental results of group screening are summarized in Table 2. As can be seen from the results, Groups, I, II, V–IX, XI, and XII yielded very low conversions ($\leqslant 6\%$) and may hence be discarded. Out of the remaining three groups, Group III possessed lower activity and selectivity as compared to Group IV and hence can be neglected. Group X (containing metal chlorides on alumina) though having the highest selectivity (96.5%) can be neglected as the activity is very low as compared to Group IV (containing fluorinated aluminas). Thus Group IV was taken up for subgroup testing.

TABLE 2
RESULTS OF GROUP SCREENING TESTS

Group	Conversion % to isobutene at 400°C and $W/F = 40$	Selectivity (%)
I	4.0	—
II	3.0	—
III	8.0	67.5
IV	27.5	87.9
V	0.5	—
VI	1.8	—
VII	2.0	—
VIII	1.2	—
IX	3.6	—
X	7.8	96.5
XI	5.1	—
XII	6.0	—

TABLE 3
EXPERIMENTAL RESULTS ON CATALYSTS OF GROUP IV

Catalyst (No.)	Catalyst	Conversion % of *n*-butene to isobutene (at 400°C and $W/F = 40$)	Selectivity %	Half-life (hr)	Activity after regeneration, as conversion %
16	η-alumina	4.1	97.0	—	—
17	Fluorinated η-alumina (0.5% F)	28.8	95.4	18.0	—
18	Fluorinated η-alumina (1% F)	33.5	87.1	62.5	33.4
19	Fluorinated η-alumina (1.5% F)	24.8	65.9	—	—
20	Fluorinated η-alumina (2% F)	20.0	49.4	—	—

The results of the tests on the constituent catalysts of Group IV are listed in Table 3 and are graphically displayed in Fig. 1. Catalysts 16, 19, and 20 can be discarded because of their very low activity (conversion). The two remaining catalysts (17 and 18) show comparable performances, and a choice has to be made between them. Catalyst 17 gives a conversion of 28.8% and selectivity of 95.4% while with Catalyst 18 the conversion and selectivity are 33.5% and 87.1% respectively. Evidently the somewhat lower conversion of Catalyst 17 is compensated by

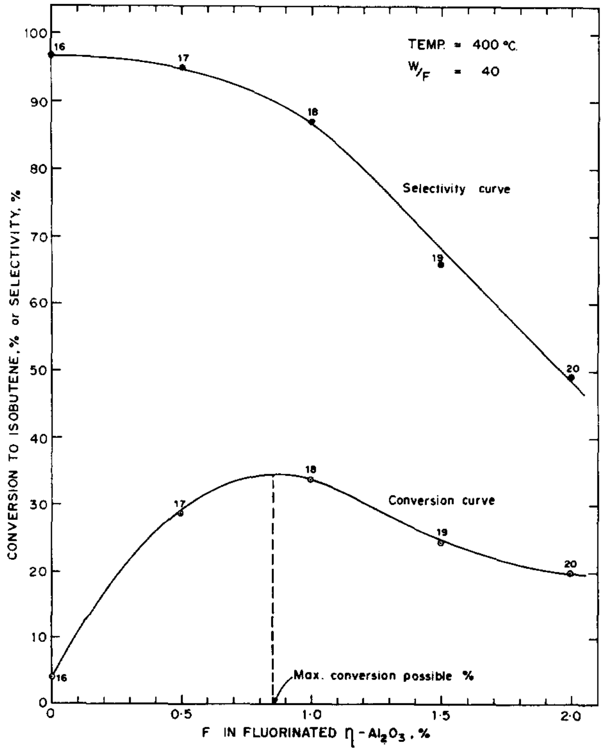


FIG. 1. Conversion and selectivity as functions of fluorine concentration in fluorinated alumina catalysts.

a slightly enhanced selectivity as compared to Catalyst 18. Life tests were, therefore, carried out on both the catalysts. The results, presented in Table 3, show that the half-life of Catalyst 18 is 62.5 hr as against 18 hr for Catalyst 17. In view of the distinctly superior performance of Catalyst 18 in this respect, regeneration tests were restricted to this catalyst only. It was found that the initial activity of the catalyst could be restored by regeneration.

It may be concluded from the results presented and discussed above that Catalyst 18 is the best among the 46 that were tested with respect to conversion, selectivity, life, and regenerability. It is also noteworthy (Fig. 1) that the conversion obtainable with this catalyst is very nearly equal to the maximum conversion possible (34.5% with 0.85% F) using fluorinated alumina catalysts.

CONCLUSION

As the first step in a comprehensive program of investigations on the catalytic isomerization of *n*-butene to isobutene, the group screening method was applied to obtain the best catalyst from among several likely candidates. Forty-six acid-solid catalysts were grouped according to their chemical similarities in 12 groups and their group performances were evaluated at 400°C and at $W/F = 40$ in an integral-type reactor. Based on the data obtained, fluorinated alumina catalysts were found to be the best and, therefore, this group of catalysts was subjected to subgroup testing, with conversion and selectivity as the main responses and life and regenerability as auxiliary responses. It was found that Catalyst 18 (fluorinated η-alumina, 1% F) was the best among all the catalysts. By employing the group screening method it was possible to identify the best catalyst in only 17 runs as against at least 46 that would have been necessary if the conventional method of testing each catalyst individually had been applied (excluding life and regeneration tests in both cases).

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