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METHOD FOR CONVERTING C_6 AND HIGHER ALIPHATIC HYDROCARBONS TO AROMATICS USING AS CATALYST A FREE ALKALI METAL ON A CARRIER

Patrick W. Ryan, Chicago Heights, Ill., assignor to Sinclair Research, Inc., Wilmington, Del., a corporation of Delaware

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The present invention relates to the conversion of C_6+ aliphatic hydrocarbons to aromatics in the presence of a novel dehydrocyclization catalyst.

The catalytic conversion of C_6+hydrocarbons to aromatics is a reaction well known to the art. In addition to producing a desirable aromatics the reaction also has particular applicability to the upgrading of low octane paraffinic feedstocks commonly available to the refiner, to higher octane motor fuel components. A variety of catalysts have been employed for this reaction, for example, noble metals on alumina, chromina-alumina, and molybdena-alumina. These and other catalysts often suggested are, however, relatively expensive and the extent of side reactions effected by many of these catalysts seriously limits the selective yields of the desired aromatics.

It has now been discovered that paraffins and/or olefins having a straight chain of at least six carbon atoms can be converted to excellent yields of aromatics by contacting them under dehydrocyclization conditions with a catalyst consisting essentially of catalytic amounts of a free alkali metal on an alkali metal ion-containing solid support. The dehydrocyclization reaction is preferably carried out at atmospheric pressure but subatmospheric and superatmospheric pressures can be employed as well. The contact time or liquid hourly space velocity will be dependent on the particular catalyst, temperature and pressure employed but will generally range from about 0.05 to 10 LHSV, preferably about 0.1 to 1 LHSV with olefin feeds and about 0.1 to 0.2 with paraffins. The temperature employed lies generally in the range of about 600 to 1000° F. but the best conditions are dependent on the feed. When paraffin feeds are used the temperature employed is preferably about 900 to 1000° F., advantageously about 950 to 990° F. Conversion temperatures employing olefin feeds on the other hand more normally range from about 600 to 1000° F., preferably about 750 to 850° F.

The feeds of the present invention can be a paraffin or monoolefin having at least six up to about 12 carbon atoms or more and include branched chain paraffins and olefins, that is, having a straight chain length of at least 6 carbon atoms. The preferred feeds are those whose straight carbon chain length is of about 8 to 10 carbon atoms. The feed converted in accordance with the method of the present invention can be the paraffins or olefins per se, admixtures of the paraffins and olefins or feeds containing the same. Particularly suitable feeds are the low octane paraffinic feedstocks such as petroleum naphtha. It has been found, moreover, that the presence of paraffins and olefins which do not have at least six straight chain carbon atoms will not unduly affect the reaction of the present invention. Likewise, the presence of aromatics and naphthenes in the feedstock have little if any detrimental effect on the conversion of the feeds of the present invention.

The catalyst of the present invention can be prepared by depositing a free alkali metal on a solid support that

contains alkali metal ions, the amount of said alkali metal ions being sufficient to at least neutralize the acidic sites on the support. The ions can be supplied by pretreatment of the support with alkali metal compounds or these compounds per se, e.g., K_2CO_3 or K_2SO_4, could even serve as the support. The pretreatment of the support can be conducted, for example, by impregnation with solutions of alkali metal compounds, as, for instance, aqueous solutions of water-soluble alkali metal compounds including alkali metal compounds that decompose under elevated temperatures as, for instance drying or calcining temperatures. Suitable alkali metal compounds include, for instance, potassium, sodium, lithium, cesium and rubidium, alcoholates, chelates, hydroxides, carbonates, bicarbonates and salts of other weak acids or salts of strong acids that are at least partially soluble or decomposable at elevated temperatures. In most cases, the pretreatment with the alkali metal compound will be followed by heating at elevated temperature which can be calcining temperature, usually about 400 to 1300° F. or more, either to decompose the alkali metal compound and/or drive-off water. The amount of alkali metal compound employed, as aforementioned, is at least sufficient to neutralize the normally acidic inert supports but amounts that provide a basic support are preferred. Whether the alkali metal ions serve as the support or are on another solid support, the resulting carrier for the free alkali metal to be added is non-acidic and is preferably baisc. Generally the amounts of alkali metal treating compounds employed on a support are those providing about 0.5 to 20%, preferably about 1 to 5%, of the alkali metal ion.

The free or elemental alkali metal constituent of the catalyst, i.e., K, Na, Li, Cs and Rb, can be dispersed on the alkali metal ion-containing support by any means known to the art. For example, the alkali metal ion-containing support can be stirred with molten alkali metal in the presence or absence of an inert solvent at a temperature slightly above the melting point of the alkali metal. A combination of alkali metals can be employed, if desired. Catalytically effective amounts of free alkali metal are used and generally fall within the range of about 1 to 20% by weight, preferably about 1 to 10% by weight, of the catalyst. The preferred alkali metal is potassium.

Although the preferred support of the present invention is alumina, other normally acidic supports such as silica, silica-alumina, acid-treated diatomaceous earth, etc. are also suitable. The alumina can be any of the variety of available alumina or alumina hydrates such as the various forms of gamma family or activated alumina, etc.

The following examples are included to further illustrate the present invention.

EXAMPLE I

A catalyst composed of 2.4 weight percent potassium metal dispersed on a 7 weight percent K+alumina support was charged to a 1" Universal reactor by adding a n-heptane-catalyst slurry under a blanket of nitrogen. The heptane was allowed to drain from the reactor and the temperature was raised to 975° F. under a slow stream of nitrogen.

A series of five runs was made on this catalyst with n-octane as the feedstock. The conditions and results of these runs are shown in Table I.

Table I

Run No. 1242	35	36	37	38	39
Conditions	975° F., Atmospheric Pressure, 0.1 LHSV				
Run time (hrs.):					
Prerun	1	1⅓	1¼	1½	1⅓
Run	5½	4¾	5⅔	6	6
Recovery g. (wt. percent):					
Liquid	79 (81.5)	60 (71.8)	67 (68.2)	69 (68.7)	74 (70.9)
Gas	11.3(11.6)	14.2(16.0)	18.4(18.6)	19.3(19.2)	17.5(16.8)
Coke [1]	4.9	6.8	9.4	8.9	8.0
Total	95.2(98.2)	81.0(96.9)	94.8(96.4)	97.2(96.7)	99.5(95.3)
Feed, g	97	83.6	98.4	100.5	104.3
F.I.A., C_5+:					
O	2.4	4.8	8.0	9.4	10.0
A	9.9	25.7	34.4	41.1	36.4
Infra-red C_5+:					
Benzene	4.45	7.67	7.81	7.46	5.93
Toluene	4.83	9.70	10.57	9.25	6.99
Ethylbenzene		26.0	7.95	13.02	13.13
p-Xylene	1.40	1.82	1.46	1.21	1.03
m-Xylene	3.19	3.74	2.75	2.21	1.75
o-Xylene	1.69	7.85	31.17	16.13	15.93
Total aromatics	15.56	33.83	43.71	49.28	44.76
Conversion, percent	39.4	63.3	71.4	79.4	77.9
Selectivity, percent	22.0	30.6	36.2	34.5	32.2

[1] The total coke on catalysts was divided proportionately over the five runs.

The data of Table I demonstrates the advantageous yields of aromatics obtained by the process of the present invention. As can be seen from the results after the catalyst comes up to activity (about 15 hrs. to 20 hrs. on stream), see Run 38, about 80 weight percent conversion of n-octane is obtained with a selectivity to aromatics of approximately 35%.

EXAMPLE II

Passage of n-hexane over a $K°/K+/Al_2O_3$ catalyst prepared as in Example I was carried out at 975° F., atmospheric pressure, and 0.1 liquid hourly space velocity. This catalyst had previously been used in runs in which n-octane and toluene were utilized as feedstocks. The results of two runs are given in Table II.

Table II

N-HEXANE OVER $K°/K+/Al_2O_3$

1242	42	43
Catalyst	$K°/K+/Al_2O_3$	$K°/K+/Al_2O_3$
Feed	n-Hexane	n-Hexane
Diluent		$H_2/HC=1$
Feed, g	79.9	50.2
Liquid recovered, g. (wt. percent)	63 (79)	41 (81.7)
Gas recovered, g	7.9	5.9
Wt. percent recovery [1]	88.8	91.6
PRODUCT DISTRIBUTION BY V.P.C.[2] AND M.S.,[3] G. PRODUCT/G. OF FEED		
H_2–C_5^-	13.9	7.8
n-C_6	49.4	34.5
Methylcyclopentane	0.8	0.6
Benzene	5.8	2.8
Toluene+	1.0	0.2
G. unaccounted for [1]	9.0	4.3

[1] Coke is not taken into account in these two figures.
[2] Vapor phase chromatography.
[3] Mass spectroscopy.

EXAMPLE III

Over the same catalyst used in Example II, 17.1 g. 2-pentene was run at 975° F., atmospheric pressure and 0.1 liquid hourly space velocity. The product consisted of 11.5 g. of liquid product and 2.1 g. of non-condensable gas. Analysis by vapor phase chromatography and mass spectroscopy showed the product to consist of hydrogen, olefins, and paraffins in the H_2–C_5 range. Only a trace of C_5+ material was produced. No evidence for cyclopentane or aromatic formation was found. Trace amounts of piperylenes were found.

EXAMPLE IV

To determine the non-catalytic behavior of hydrocarbons such as n-octane under these conditions a thermal run was made at 975° F., atmospheric pressure, and 0.1 liquid hourly space velocity with tabular alumina in place of the catalyst. A 99.9 weight percent recovery was obtained. Analysis of the product showed 87% to be unreacted n-octane, 0.3% toluene, 0.6% benzene and the remainder lower molecular weight hydrocarbons.

EXAMPLE V

Passage of 42 g. of o-xylene over the $K°/K+/Al_2O_3$ catalyst of Example I, which had previously been used to process octane feedstock, at 900° F., atmospheric pressure, 0.2 LHSV with a nitrogen diluent resulted in the recovery of 38 g. of material which was essentially unchanged o-xylene.

EXAMPLE VI

Passage of 28 g. of methylcyclopentane over the same catalyst and under the same conditions as Example V resulted in the recovery of 24 g. of liquid product. Except for trace amounts of probably methylcyclopentene the product was unchanged starting material.

EXAMPLE VII

A catalyst composed of 2.4% K metal dispersed on a 7 weight percent $K+/Al_2O_3$ support was charged to a 1" Universal reactor by passing a n-heptane catalyst slurry under a blanket of nitrogen. The heptane was drained and the catalyst brought to reaction temperature under a slow stream of nitrogen.

A series of four runs (Runs 29–32) in which mixed n-octenes were utilized as feedstock was carried out. The reaction was followed by taking grab samples at various times during each run to note the change in product distribution. No attempt was made to trap out condensable gases. The estimated liquid recovery range is about 85–90%.

Analyses of the grab samples for these runs are shown in Table III. From the results shown, this catalyst system has high activity for the conversion of octenes to aromatics. Based on vapor phase chromotography of the grab samples, there is a 63% by weight conversion of the olefin to 61.5 weight percent aromatics. The selectivity to C_8 aromatics is also quite high. The catalyst

appears to age after the first hour and then levels off with only a slow rate of aging.

EXAMPLE VIII

A further run (Run 38) was made in which 34.3 g. of 1-octene was passed over the catalyst of Example VII after it had been used in runs in which methylcyclopentane, o-xylene and n-octane were employed as feedstock. The conditions for this run were the same as those cited in Example VII except that the temperature was raised to 900° F. 28 g. of liquid product and 0.23 ft.^{3} of gas were collected. Vapor phase analyses of the liquid product is also shown in Table III as can be seen from these results, the catalyst, although it becomes less selective with catalyst age, is still quite active for this dehydrocyclization reaction.

Table III

Run	29			30		31		32		38
Conditions	Atmospheric Pressure, 0.2 LHSV, N_2 diluent (2/1 N_2/HC mole ratio)									
Temp., ° F	800			800		800		875		900
Analyses of grab samples by V.P.C.[1]										
Time (min.)	0–15	15–60	60–120	0–15	15–120	0–15	15–60	0–15	15–60	
C_2										
C_3	T			T	T			T	T	1.2
C_4	T	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.3	4.0
C_5	0.1	0.2	0.3	0.2	0.3	0.3	0.3	0.8	0.9	5.3
C_6	0.2	0.5	0.6	0.5	0.3	0.6	0.3	0.9	1.2	3.0
ϕH		0.3	0.5	0.5	0.5	0.8	0.8	2.5	2.4	4.2
C_7	1.4	4.0	2.7	2.7	0.5	0.9	0.5	1.0	1.4	2.0
ϕCH_3	4.2	4.2	3.5	3.9	2.5	1.5	2.6	8.2	7.4	5.8
C_8 / Other C_8[2]	36.8	39.0	62.4	60.4	76.2	81.9	83.3	47.9	54.0	42.7
$Et\phi$	2.1	4.3	2.7	2.9	1.8	1.8	1.4	6.7	5.6	10.0
m+p-Xylene	16.0	27.6	18.5	19.0	11.7	7.5	6.2	17.9	4.3	5.2
o-Xylene	39.2	19.8	8.7	9.8	6.1	4.7	4.5	13.9	12.5	16.6
Infra-red analyses:										
Benzene					0.62					
Toluene	4.09	3.24			3.90					
Ethylbenzene	0.73	5.29			5.03					
m-Xylene	7.32	22.40			9.41					
p-Xylene	9.12	10.55			5.24					
o-Xylene	39.04	19.74			7.72					
Gas make, ft.^{3}/hr	0.97		0.38	0.36	0.27	0.22	0.21	0.50	0.50	

[1] No attempt was made to differentiate between the paraffins and olefins of each carbon number.
[2] Probably C_8 naphthenes.

I claim:

1. A method for the conversion of C_6 plus aliphatic hydrocarbons to aromatics which comprises contacting a feedstock selected from the group consisting of paraffins and monoolefins having a straight carbon chain length of at least six carbon atoms under dehydrocyclization conditions with a catalyst consisting essentially of catalytically effective amounts of a free alkali metal on a solid, acidic catalyst support selected from the group consisting of silica, alumina, and mixtures thereof containing sufficient alkali metal ions, to provide a non-acidic support.

2. The method of claim 1 wherein the feedstock is an olefin of 6 to 12 total carbons and the dehydrocyclization conditions include temperatures of about 600 to 1000° F.

3. The method of claim 1 wherein the feedstock is a paraffin of 6 to 12 carbon atoms and the dehydrocyclization conditions include temperatures of about 900 to 1000° F.

4. The method of claim 1 wherein the amount of free alkali metal on the support is about 1 to 20% by weight and the amount of alkali metal ion is about 0.5 to 20%.

5. The method of claim 2 wherein the alkali metal is potassium.

6. The method of claim 5 wherein the catalyst support is alumina.

7. The method of claim 6 wherein the feedstock is octene.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*