

PATENT SPECIFICATION

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(54) PREPARATION OF AROMATICS

(71) We, MOBIL OIL CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It has long been known to contact various hydrocarbon fractions with acidic catalysts generally and, in particular, with solid siliceous acidic catalysts—including those referred to as crystalline aluminosilicate zeolites. Contact of the hydrocarbon feed with acid catalysts was carried out for a wide variety of reactions including cracking, isomerization and hydrocracking. Representative United States Patents disclosing and claiming contacting of various hydrocarbon fractions with crystalline aluminosilicates are United States Patents Nos. 3,140,249; 3,140,251; 3,140,253; and 3,140,322.

The contact of paraffinic feedstocks with crystalline aluminosilicate zeolites is also known in the art and by far the primary reason for contacting paraffinic materials with zeolites has been for the purpose of cracking them, i.e. converting them to lower molecular weight products. Typical applications in this general field would be the use of crystalline aluminosilicate zeolites for carrying out dewaxing reactions, i.e. the cracking of paraffins to low molecular weight materials. United States Patent 3,400,072 discloses a dewaxing process with crystalline aluminosilicates generally.

The present application is not concerned with hydrocarbon conversion in general, but rather, is concerned with the conversion of hydrocarbons consisting essentially of C_2 — C_4 paraffins, olefins, and mixtures thereof. Additionally, the present application is not concerned with any hydrocarbon conversion such as the cracking of these materials to still lower molecular weight products, but rather, is concerned with the preparation of aromatic com-

pounds from C_2 — C_4 olefins, paraffins, and mixtures thereof.

The formation of aromatic compounds from low molecular weight paraffins is also known in the art, but the prior processes always required the presence of a strong hydrogenation/dehydrogenation component. Processes of this type are disclosed in United States Patents Nos. 3,296,234 and 3,374,281.

According to the present invention aromatic compounds are formed by contacting a feed stream of C_2 — C_4 paraffins, olefins or a mixture thereof with a crystalline aluminosilicate:

- (i) having a silica-to-alumina ratio greater than 15;
- (ii) crystallized from a solution containing organic cations so that it contains organic cations as synthesized; and
- (iii) having a pore size such that it sorbs methyl paraffins at the conditions employed; these conditions comprising
 - (a) a temperature of 100 to 700°C;
 - (b) a pressure of 0 to 100 p.s.i.g.;
 - (c) a WHSV of 0.5 to 400; and
 - (d) a hydrogen/hydrocarbon ratio of 0 to 20.

The term 'methyl paraffin' refers to a paraffin having a methyl group as the only side chain. It appears that a novel reaction mechanism is involved since for the first time it is not necessary to employ a hydrogenation/dehydrogenation component in association with the crystalline aluminosilicate zeolite.

The process of this invention has a very practical economic potential since catalysts employed are surprisingly stable under the reaction conditions employed so that they remain active over long periods of time thereby eliminating the need for frequent regeneration. As can well be appreciated, a common characteristic of all prior acidic catalysts, whether amorphous or crystalline, was that they aged rapidly in the absence of a hydrogenation/dehydrogenation component. The present invention provides a process for the direct conversion of C_2 — C_4 paraffins or olefins to aromatics which can be operated for long periods

of time without adverse effects on catalyst activity or product selectivity.

The process of this invention may be carried out using catalysts comprising crystalline aluminosilicates of which the following are examples:

I. Zeolites of the so-called "ZSM-5 type", which type includes zeolites ZSM-5 (described in United States Patent No. 3,702,886), ZSM-8 (described in German Offenlegungsschrift No. 2,049,755) and ZSM-11 (described in United States Patent No. 3,709,979);

II. Zeolite beta (described in United States Patent No. 3,308,069);

III. Zeolite ZSM-12 (described in German Offenlegungsschrift No. 2,213,109); and

IV. Mordeite synthesized via a reaction mixture which contains tetraethylammonium cations.

The zeolites used in the present invention usually have the original cations associated therewith replaced by a wide variety of other cations according to techniques well known in the art. Typical replacing cations include hydrogen, ammonium and metal cations including mixtures of the same. Of the replacing cations, particular preference is given to cations of hydrogen, ammonium, rare earth, and mixtures thereof.

Typical ion exchange techniques would be to contact the particular zeolite with a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, particular preference is given to chlorides, nitrates and sulfates.

Representative ion exchange techniques are disclosed in a wide variety of patents including United States Patents Nos. 3,140,249; 3,140,251; and 3,140,253.

Following contact with the salt solution of the desired replacing cation, the zeolites may be washed with water and dried at a temperature ranging from 150°F to 600°F and thereafter heated in air or other inert gas at temperatures ranging from 500°F to 1500°F for periods of time ranging from 1 to 48 hours or more.

It is also possible to treat the zeolite with steam at elevated temperatures ranging from 800°F to 1600°F and preferably 1000°F and 1500°F, if such is desired. The treatment may be accomplished in atmospheres consisting partially or entirely of steam.

A similar treatment can be accomplished at lower temperatures and elevated pressures, e.g. 350–700°F at 10 to 200 atmospheres.

One embodiment of this invention resides in the use of a porous matrix together with the ZSM-5 type zeolite previously described. The ZSM-5 type zeolite can be combined, dispersed or otherwise intimately admixed with a porous matrix in such proportions that the resulting product contains from 1% to 95% by weight, and preferably from 50 to 80%

by weight, of the zeolite in the final composite.

The term "porous matrix" includes inorganic compositions with which the aluminosilicates can be combined, dispersed or otherwise intimately admixed wherein the matrix may be active or inactive. It is to be understood that the porosity of the compositions employed as a matrix can either be inherent in the particular material or it can be introduced by mechanical or chemical means. Representative matrices which can be employed include metals and alloys thereof, sintered metals and sintered glass, asbestos, silicon carbide aggregates, pumice, firebrick, diatomaceous earths, and inorganic oxides. Inorganic compositions especially those of a siliceous nature are preferred. Of these matrices, inorganic oxides such as clay, chemically treated clay, silica or silica-alumina, are particularly preferred because of their superior porosity, attrition resistance, and stability.

The compositing of the aluminosilicate with an inorganic oxide can be achieved by several methods wherein the aluminosilicates are reduced to a particle size less than 40 microns, preferably less than 10 microns, and intimately admixed with an inorganic oxide while the latter is in a hydrous state such as in the form of hydrosol, hydrogel, wet gelatinous precipitate, or in a dried state, or a mixture thereof. Thus, finely divided aluminosilicates can be mixed directly with a siliceous gel formed by hydrolyzing a basic solution of alkali metal silicate with an acid such as hydrochloric, sulfuric or acetic. The mixing of the three components can be accomplished in any desired manner, such as in a ball mill or other types of mills. The aluminosilicates may also be dispersed in a hydrosol obtained by reacting an alkali metal silicate with an acid or alkaline coagulant. The hydrosol is then permitted to set in mass to a hydrogel which is thereafter dried and broken into pieces of desired shape or dried by conventional spray drying techniques or dispersed through a nozzle into a bath of oil or other water-immiscible suspending medium to obtain spheroidally shaped "bead" particles of catalyst such as described in United States Patent No. 2,384,946. The aluminosilicate siliceous gel thus obtained is washed free of soluble salts and thereafter dried and/or calcined as desired.

In a like manner, the aluminosilicates may be incorporated with an aluminiferous oxide. Such gels and hydrous oxides are well known in the art and may be prepared, for example by adding ammonium hydroxide or ammonium carbonate to a salt of aluminium, such as aluminium chloride, aluminium sulfate or aluminium nitrate, in an amount sufficient to form aluminium hydroxide which, upon drying, is converted to alumina. The aluminosilicate may be incorporated with the aluminifer-

ous oxide while the latter is in the form of hydrosol, hydrogel, or wet gelatinous precipitate or hydrous oxide, or in the dried state.

5 The catalytically active inorganic oxide matrix may also consist of a plural gel comprising a predominant amount of silica with one or more metals or oxides thereof from Group IB, II, III, IV, V, VI, VII, or VIII of the
10 Periodic Table. Particular preference is given to plural gels or silica with metal oxides of Groups IIA, III and IVa of the Periodic Table, especially wherein the metal oxide is rare earth oxide, magnesia, alumina, zirconia,
15 titania, beryllia, thorina, or combination thereof. The preparation of plural gels is well known and generally involves either separate precipitation or coprecipitation techniques, in which a suitable salt of the metal oxide is
20 added to an alkali metal silicate and an acid or base, as required, is added to precipitate the corresponding oxide. The silica content of the siliceous gel matrix contemplated herein is generally within the range of 55 to 100
25 weight percent with the metal oxide content ranging from 0 to 45 percent.

The inorganic oxide may also consist of raw clay or a clay mineral which has been treated with an acid medium to render it
30 active. The aluminosilicate can be incorporated into the clay simply by blending the two and fashioning the mixture into desired shapes. Suitable clays include attapulgite, kaolin, sepiolite, polygarskite, kaolinite, hallosite, plastic ball clays, bentonite, montmorillonite, illite
35 and chlorite.

Other useful matrices include powders of refractory oxides, such as alumina and alpha alumina, having very low internal pore volume.
40 Preferably, these materials have substantially no inherent catalytic activity of their own.

The catalyst can be heated in steam or in other atmospheres, e.g. air, near the temperature contemplated for conversion but may be heated to operating temperatures initially during use in the conversion process. Generally,
45 the catalyst is dried between 150°F and 600°F and thereafter may be calcined in air, steam, nitrogen, helium, flue gas or other gases not harmful to the catalyst at temperatures ranging from 500°F to 1600°F for periods of time
50 ranging from 1 to 48 hours or more. It is to be understood that the aluminosilicate can also be calcined prior to incorporation into the inorganic oxide gel. It is also to be understood that the aluminosilicate or aluminosilicates need not be ion exchanged prior to incorporation in a matrix but can be so treated during or after incorporation in a matrix.
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60 The process of this invention is carried out simply by contacting the feed stream of C_1-C_4 paraffins and/or olefins (ethane, propane, butane, isobutane, ethylene, propylene, butene, isobutene, and mixtures thereof) with a zeolite of the kind previously defined at a temperature

from 100—700°C and recovering the aromatics produced. The reaction can take place at atmospheric pressure and in the absence of added hydrogen. The aromatics which are produced are predominantly C_6-C_{10} aromatics.

70 It is to be immediately understood, however, that although the invention has been described with reference to the fact that it is not necessary to use a hydrogenation/dehydrogenation component, nor is it necessary to carry out the reaction in the presence of added hydrogen, nevertheless both these features can be employed if such is desired. It might very well be, for example, that the presence of a
75 hydrogenation component might have a beneficial effect on the catalyst in that it might add even further to its stability by hydrogenating coke preformers as is well known in the art. As has been previously stressed, the prior art processes absolutely required hydrogen and required the presence of a strong hydrogenation component, whereas the process of this invention does not. However, the scope of the invention is not departed from by the mere
80 addition of hydrogenation component to the zeolite catalysts and/or the matrix when such is used, nor by the mere addition of hydrogen. It is to be understood, however, that the preferred embodiment of this invention resides in operating in the absence of hydrogen and in the absence of a hydrogenation component.

When a hydrogenation/dehydrogenation component is used it need not be a "strong hydrogenation component" but can be any
85 hydrogenation component conventionally known in the art. These components can include metals, oxides, and sulfides of metals of the Periodic Table which fall in Group VIB including chromium, molybdenum and tungsten; Group IIB including zinc and cadmium, Group VIIB including manganese and rhenium and Group VIII including cobalt, nickel, platinum, palladium, ruthenium, and rhodium, and combinations of metals, sulfides and oxides
90 of metals of Group VIB and VIII, such as nickel-tungsten-sulfide and cobalt oxide, molybdenum oxide.

Thus, the processing conditions envisaged in the operation of the present process have temperatures ranging from 100 to 700°C, pressure ranging from 0—1,000 lbs psig, hydrogen to hydrocarbon ratios are from 0—20 and WHSV from 0.1 to 500. Preferred operating conditions are temperatures from 300 to
95 650°C, pressure atmospheric to 300 lbs/psig, absence of hydrogen and WHSV from 0.5 to 400.

The following Examples illustrate the best mode contemplated for carrying out this invention.

EXAMPLES 1—4

100 Examples 1—4 illustrate the preparation of C_6+ aromatics by contacting propylene at various temperatures with a catalyst compo-

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sition consisting of 80 parts by weight of H-ZSM-5 (prepared according to the procedure disclosed in Example 5 of U.K. Specification No. 1,323,710) and 20 parts by weight of alumina. The catalyst composition contained

no hydrogenation/dehydrogenation component and no added hydrogen was used. All runs were at atmospheric pressure.

Additional operating conditions and results are shown in the following Table.

	Charge WHSV	Propylene—7.72 g			
		3.9	300	400	500
	Temperature (°C)	200	300	400	500
	Product Recovery (Wt %)				
15	Total Product (−196°)	99	96	96	95
	Liquid Product (0°)	59	61	52	55
	Product Yield (g/100 C ₃ H ₆)				
	P+O+N	44.0	35.5	12.5	2.8
20	C ₆ Aromatics	2.9	1.1	2.0	10.4
	C ₇ Aromatics	3.5	6.3	23.3	35.9
	C ₈ Aromatics	3.8	6.0	9.2	4.0
	C ₉ + Aromatics	5.1	12.5	4.5	2.1
	Liquid Product	59	61	52	55
25	C ₆ + Aromatics	15	26	39	52
	C ₂ —C ₄ Olefins	31	4	8	17
	Aromatics and Olefins	46	30	47	69

EXAMPLE 5

This Example will illustrate that it is possible to use added weak hydrogenation/dehydrogenation components.

In this Example, the catalyst employed was an ammonium and zinc exchanged ZSM-5 (Zn/HZSM-5) (prepared in accordance with Example 7 of U.K. Specification No. 1,323,710). The reaction took place at 500°C in the absence of added hydrogen and at a pressure of one atmosphere.

Results are shown in the following Table:

40	Propane (g)	3.4
	Total Cond. Prod. (g) (−196°C)	1.877
	Total Liquid Prod. (g)	.347
	GLC Analysis (Wt %)	
45	Paraffins and Olefins	0.9
	C ₆ —Aromatics	48.6
	C ₇ —Aromatics	39.6
	C ₈ —Aromatics	7.1
	C ₉ +—Aromatics	2.5
50	Aromatics (C ₆ —C ₉) (g)	.348
	Wt % of Charge	10
	Heavy Gas	
	Wt (g)	1.53
	Analysis M.S.	
55	Olefins (C ₂ —C ₄) (Wt %)	12
	Paraffins (Wt %)	87
	Olefins (C ₂ —C ₄) (g)	0.184
	Wt % of Charge	5
	Olefins Plus Aromatics	
60	Wt % of Charge	15

WHAT WE CLAIM IS:—

1. A process for producing aromatic compounds which comprises contacting C₂—C₄ paraffins, olefins or mixtures thereof with a crystalline aluminosilicate zeolite (i) having a silica-to-alumina ratio greater than 15; (ii) crystallized from a solution containing organic cations so that it contains organic cations as synthesized; and (iii) having a pore size such that it sorbs methyl paraffins at the conditions employed; these conditions comprising (a) a temperature of 100 to 700°C; (b) a pressure of 0 to 1000 p.s.i.g.; (c) a WHSV of 0.5 to 400; and (d) a hydrogen-hydrocarbon ratio of 0 to 20.
2. A process according to Claim 1, wherein the temperature employed is 300 to 650°C.
3. A process according to Claim 1, or 2, which is carried out at atmospheric pressure and in the absence of added hydrogen.
4. A process according to any preceding claim wherein said zeolite has been base exchanged with hydrogen or ammonium cations.
5. A process according to any of Claims 1 to 4 wherein said zeolite is a zeolite of the ZSM-5 type.
6. Process of preparing aromatic compounds substantially as described in any of the foregoing Examples.

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sition consisting of 80 parts by weight of H-ZSM-5 (prepared according to the procedure disclosed in Example 5 of U.K. Specification No. 1,323,710) and 20 parts by weight of alumina. The catalyst composition contained

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	Liquid Product (0°)	59	61	52	55
20	Product Yield (g/100 C ₃ H ₆)				
	P+O+N	44.0	35.5	12.5	2.8
	C ₆ Aromatics	2.9	1.1	2.0	10.4
	C ₇ Aromatics	3.5	6.3	23.3	35.9
	C ₈ Aromatics	3.8	6.0	9.2	4.0
25	C ₉ + Aromatics	5.1	12.5	4.5	2.1
	Liquid Product	59	61	52	55
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	C ₉ +—Aromatics	2.5
50	Aromatics (C ₆ —C ₉) (g)	348
	Wt % of Charge	10
	Heavy Gas	
	Wt (g)	1.53
	Analysis M.S.	
55	Olefins (C ₂ —C ₄) (Wt %)	12
	Paraffins (Wt %)	87
	Olefins (C ₂ —C ₄) (g)	0.184
	Wt % of Charge	5
	Olefins Plus Aromatics	
60	Wt % of Charge	15

WHAT WE CLAIM IS:—

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5. A process according to any of Claims 1 to 4 wherein said zeolite is a zeolite of the ZSM-5 type.
6. Process of preparing aromatic compounds substantially as described in any of the foregoing Examples.

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