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(54) Title: CATALYTIC HYDRODEALKYLATION OF AROMATICS

(57) Abrégé/Abstract:

A process is provided for hydrodealkylation of alkylaromatic hydrocarbons to produce benzene or BTX over catalyst comprising nickel or a noble metal and a synthetic zeolite, having in its calcined form, an X-ray diffraction pattern including interplanar d-spacings at 12.36 ± 0.4 , 11.03 ± 0.2 , 8.83 ± 0.14 , 6.18 ± 0.12 , 6.00 ± 0.10 , 4.06 ± 0.07 , 3.91 ± 0.07 and 3.42 ± 0.06 Angstroms.



ABSTRACTCATALYTIC HYDRODEALKYLATION OF AROMATICS

5 A process is provided for hydrodealkylation of alkylaromatic hydrocarbons to produce benzene or BTX over catalyst comprising nickel or a noble metal and a synthetic zeolite, having in its calcined form, an X-ray diffraction pattern including interplanar d-spacings at 12.36 ± 0.4 , 11.03 ± 0.2 , 8.83 ± 0.14 , 6.18 ± 0.12 , 6.00 ± 0.10 , 4.06 ± 0.07 , 3.91 ± 0.07 and 3.42 ± 0.06 Angstroms.

CATALYTIC HYDRODEALKYLATION OF AROMATICS

This invention relates to the catalytic hydrodealkylation of alkylaromatic compounds to produce a product containing benzene, toluene, and xylene.

Hydrodealkylation (HDA) has been used to convert alkylaromatics to BTX (benzene, toluene, and xylene). Benzene is an especially desired product because of its high demand. Conversely, C_9+ aromatics have relatively low value as compared with benzene.

Thermal HDA has been used to convert C_7/C_8 alkylaromatics to benzene, and remains as an important technology for benzene production in many developing countries. Some studies have indicated that the conventional thermal HDA process can be modified so as to use a C_9+ feedstock (see Oil and Gas Journal, March 20, 1989, pp. 91 to 99).

U.S. Patent No. 4,341,662 discloses BTX production from heavy reformat in substantially the portion in said reformat of single ring aromatics bearing none, one, or two methyl groups by contacting the heavy reformat at $427-540^{\circ}\text{C}$ ($800-1000^{\circ}\text{F}$) with a zeolite of low acid activity.

The present invention relates to a process for catalytic hydrodealkylation of a hydrocarbon feedstock containing alkylaromatic compounds to provide a hydrodealkylated product containing benzene, said process comprising contacting said feedstock with a catalyst composition comprising a noble metal or nickel and a synthetic zeolite characterized by an X-ray diffraction pattern including values set forth in Table A below.

In the present process, a feedstock containing C_9^{+} aromatics can be catalytically hydrodealkylated to produce BTX or benzene alone. The feedstock ideally

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has a high aromatics content to simplify product separation. The feedstock to the present process may, for example, comprise greater than about 50 mole% C_6 - C_{12} single-ring aromatics. It may comprise greater than about 50 mole% C_9 - C_{12} single-ring aromatics.

The process of the present invention is flexible in its capacity to use different feed compositions. For example, the feedstock may be derived from the gasoline produced by the light cycle oil (LCO) upgrading processes such as described in U.S. Patent Nos. 4,789,457; 4,738,766; and 4,676,887, and it may include saturates. Conversion and selectivity of the catalytic process of the present invention exceeds that of thermal hydrodealkylation under the same conditions.

The process of the present invention comprises contacting a feed containing, for example, C_9 + aromatics with a synthetic porous crystalline catalyst in the presence of hydrogen under hydrodealkylation conditions. Preferably the hydrodealkylation conditions include a temperature of 315 to 540°C (600 to 1000°F), a pressure of 445 to 3550 kPa (50 to 500 psig), a hydrogen circulation rate of 89 to 890 Nm^3/m^3 (500 to 5000 scf/bbl), preferably 90 to 360 Nm^3/m^3 , and a liquid hourly space velocity (LHSV) of 0.5 to 10 hr^{-1} .

The catalyst employed herein comprises a noble metal or nickel and a crystalline zeolite characterized by an X-ray diffraction pattern including the interplanar d-spacings of Table A. Such a catalyst is much more active and more selective than thermal HDA for benzene production from heavy aromatics. The presence of nickel or a noble metal, preferably platinum or palladium, hydrogenates olefins generated by the dealkylation reactions and thus minimizes the recombination of olefins with the BTX. The present catalyst dealkylates alkylbenzenes regardless of chain

length, and preserves its activity while processing feeds of lower aromatics content.

In its calcined form, the zeolite employed in the process of this invention is characterized by an X-ray diffraction pattern including the following lines:

TABLE A

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
12.36 $\pm$ 0.4	M-VS
11.03 $\pm$ 0.2	M-S
8.83 $\pm$ 0.14	M-VS
6.18 $\pm$ 0.12	M-VS
6.00 $\pm$ 0.10	M-M
4.06 $\pm$ 0.07	W-S
3.91 $\pm$ 0.07	M-VS
3.42 $\pm$ 0.06	VS

In one preferred embodiment, the calcined form of the zeolite is characterized by an X-ray diffraction pattern including the following lines:

TABLE B

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
30.0 $\pm$ 2.2	W-M
22.1 $\pm$ 1.3	W
12.36 $\pm$ 0.4	M-VS
11.03 $\pm$ 0.2	M-S
8.83 $\pm$ 0.14	M-VS
6.18 $\pm$ 0.12	M-VS
6.00 $\pm$ 0.10	W-M
4.06 $\pm$ 0.07	W-S
3.91 $\pm$ 0.07	M-VS
3.42 $\pm$ 0.06	VS

In another preferred embodiment, the calcined form of the zeolite is characterized by an X-ray diffraction pattern including the following lines:

TABLE C

	<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
5	12.36 $\pm$ 0.4	M-VS
	11.03 $\pm$ 0.2	M-S
	8.83 $\pm$ 0.14	M-VS
	6.86 $\pm$ 0.14	W-M
10	6.18 $\pm$ 0.12	M-VS
	6.00 $\pm$ 0.10	W-M
	5.54 $\pm$ 0.10	W-M
	4.92 $\pm$ 0.09	W
	4.64 $\pm$ 0.08	W
15	4.41 $\pm$ 0.08	W-M
	4.25 $\pm$ 0.08	W
	4.10 $\pm$ 0.07	W-S
	4.06 $\pm$ 0.07	W-S
	3.91 $\pm$ 0.07	M-VS
20	3.75 $\pm$ 0.06	W-M
	3.56 $\pm$ 0.06	W-M
	3.42 $\pm$ 0.06	VS
	3.30 $\pm$ 0.05	W-M
	3.20 $\pm$ 0.05	W-M
25	3.14 $\pm$ 0.05	W-M
	3.07 $\pm$ 0.05	W
	2.99 $\pm$ 0.05	W
	2.82 $\pm$ 0.05	W
	2.78 $\pm$ 0.05	W
30	2.68 $\pm$ 0.05	W
	2.59 $\pm$ 0.05	W

Most preferably, the calcined form of the zeolite is characterized by an X-ray diffraction pattern including the following lines:

TABLE D

	<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
5	30.0 $\pm$ 2.2	W-M
	22.1 $\pm$ 1.3	W
	12.36 $\pm$ 0.4	M-VS
	11.03 $\pm$ 0.2	M-S
10	8.83 $\pm$ 0.14	M-VS
	6.86 $\pm$ 0.14	W-M
	6.18 $\pm$ 0.12	M-VS
	6.00 $\pm$ 0.10	W-M
	5.54 $\pm$ 0.10	W-M
15	4.92 $\pm$ 0.09	W
	4.64 $\pm$ 0.08	W
	4.41 $\pm$ 0.08	W-M
	4.25 $\pm$ 0.08	W
	4.10 $\pm$ 0.07	W-S
20	4.06 $\pm$ 0.07	W-S
	3.91 $\pm$ 0.07	M-VS
	3.75 $\pm$ 0.06	W-M
	3.56 $\pm$ 0.06	W-M
	3.42 $\pm$ 0.06	VS
25	3.30 $\pm$ 0.05	W-M
	3.20 $\pm$ 0.05	W-M
	3.14 $\pm$ 0.05	W-M
	3.07 $\pm$ 0.05	W
	2.99 $\pm$ 0.05	W
30	2.82 $\pm$ 0.05	W
	2.78 $\pm$ 0.05	W
	2.68 $\pm$ 0.05	W
	2.59 $\pm$ 0.05	W

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper and a diffractometer equipped with a scintillation counter and an associated computer was used. The peak heights, I , and the positions as a function of 2θ , where θ is the Bragg angle, were determined using algorithms on the computer associated with the diffractometer. From these, the relative intensities, $100 I/I_0$, where I_0 is the intensity of the strongest line or peak, and d (obs.) the interplanar spacing in Angstrom Units (A), corresponding to the recorded lines, were determined. In Tables A-D, the relative intensities are given in terms of the symbols W=weak, M=medium, S=strong, VS=very strong. In terms of intensities, these may be generally designated as follows:

W = 0-20

M = 20-40

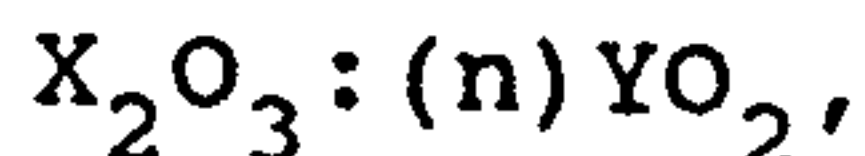
S = 40-60

VS = 60-100

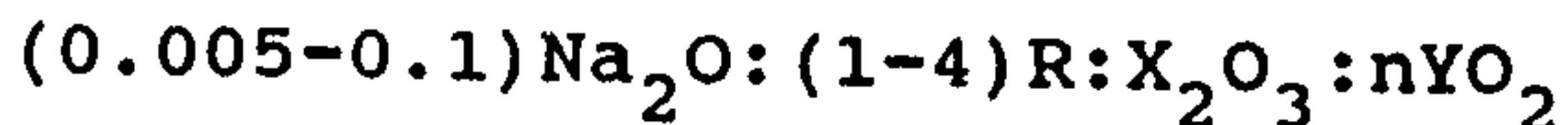
It should be understood that these X-ray diffraction patterns are characteristic of all species of the zeolite. The sodium form as well as other cationic forms reveal substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the ratio of structural components, e.g., silicon to aluminum mole ratio of the particular sample, as well as its degree of thermal treatment.

Examples of zeolites with X-ray patterns according to Table A include the PSH-3 composition of U.S. Patent No. 4,439,409, and MCM-22 described in U.S. Patent No. 4,954,325.

Zeolite MCM-22 has a composition involving the molar relationship:



wherein X is a trivalent element, such as aluminum, boron, iron and/or gallium, preferably aluminum, Y is a tetravalent element such as silicon and/or germanium, preferably silicon, and n is at least 10, usually from 10 to 150, more usually from 10 to 60, and even more usually from 20 to 40. In the as-synthesized form, zeolite MCM-22 has a formula, on an anhydrous basis and in terms of moles of oxides per n moles of YO_2 , as follows:



wherein R is hexamethyleneimine. The Na and R components are associated with the zeolite as a result of their presence during crystallization, and are easily removed by post-crystallization methods hereinafter more particularly described.

In its calcined form, zeolite MCM-22 appears to be made up of a single crystal phase with little or no detectable impurity crystal phases and has an X-ray diffraction pattern including the lines listed in above Tables A-D.

Zeolite MCM-22 can be prepared from a reaction mixture containing sources of alkali or alkaline earth metal (M), e.g., sodium or potassium, cation, an oxide of trivalent element X, e.g., aluminum, an oxide of tetravalent element Y, e.g., silicon, an organic directing agent (R), in the form of hexamethyleneimine, and water, said reaction mixture having a composition, in terms of mole ratios of oxides, within the following ranges:

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	<u>Reactants</u>	<u>Useful</u>	<u>Preferred</u>
	$\text{YO}_2/\text{X}_2\text{O}_3$	10 - 60	10 - 40
	$\text{H}_2\text{O}/\text{YO}_2$	5 - 100	10 - 50
	OH^-YO_2	0.01 - 1.0	0.1 - 0.5
5	M/YO_2	0.01 - 2.0	0.1 - 1.0
	R/YO_2	0.05 - 1.0	0.1 - 0.5

In a preferred method of synthesizing zeolite MCM-22, the YO_2 reactant contains a substantial amount of solid YO_2 , e.g., at least about 30. wt.% solid YO_2 . Where YO_2 is silica, the use of a silica source containing at least about 30 wt.% solid silica, e.g., UltrasilTM (a precipitated, spray dried silica containing about 90 wt.% silica) or HiSilTM (a precipitated hydrated SiO_2 containing about 87 wt.% silica, about 6 wt.% free H_2O and about 4.5 wt.% bound H_2O of hydration and having a particle size of about 0.02 micron) favors MCM-22 crystal formation from the above mixture. If another source of oxide of silicon, e.g., Q-Brand (a sodium silicate comprising about 28.8 wt.% SiO_2 , 8.9 wt.% Na_2O and 62.3 wt.% H_2O) is used, crystallization may yield impurity phases of other crystal structures. Preferably, therefore, the YO_2 , e.g., silica, source contains at least about 30 wt.% solid YO_2 , e.g., silica, and more preferably at least about 40 wt.% solid YO_2 , e.g., silica.

Crystallization of the MCM-22 crystalline material can be carried out under either static or stirred conditions in a suitable reactor vessel such as, e.g., polypropylene jars or teflon-lined or stainless steel autoclaves at a temperature of 80 to 225°C for a time of 25 hours to 60 days. Thereafter, the crystals are separated from the liquid and recovered.

5 In the catalyst used in the process of the invention, it may be desirable to incorporate the crystalline zeolite material with another material, i.e., a binder, which is resistant to the temperatures and other conditions employed in the process of this invention. Suitable binder materials include active and inactive materials and synthetic or naturally occurring zeolite as well as inorganic materials such as clays, silica and/or metal oxides such as alumina. 10 The latter can be either naturally occurring or provided in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Use of a binder material in conjunction with the zeolite, i.e., combined therewith or present during its 15 synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitable serve as diluents to control the amount of conversion so that products can be obtained economically and in a 20 controlled fashion without having to employ other means for controlling the rate of reaction.

25 These materials can be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the zeolite under commercial operating conditions. Good crush strength is an advantageous attribute for commercial use since it prevents or delays breaking down of the catalyst into powder-like materials.

30 Naturally occurring clays which can be composited with the zeolite crystals include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolines commonly known as Dixie, McNamee, Georgia and Florida clays or others in which the main mineral constituent is halloysite, 35 kaolinite, dickite, nacrite, or anauxite. Such clays

can be used in the raw state as originally mined or initially subjected to calcination, acid treatment or chemical modification. Binders useful for compositing with the zeolite also include inorganic oxides, notably alumina.

Apart from or in addition to the foregoing binder materials, the zeolite crystals can be composited with an organic oxide matrix such as silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, silica-magnesia-zirconia, etc. It may also be advantageous to provide at least a part of the foregoing matrix materials in colloidal form so as to facilitate extrusion of the bound catalyst component(s).

The relative proportions of zeolite and inorganic oxide matrix can vary widely with the zeolite content ranging from 1 to 95 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

The stability of the zeolite catalyst may be increased by steaming, with suitable steam stabilization conditions including contacting the catalyst with, for example, 5-100% steam at a temperature of at least 300°C (e.g. 300-650°C) for at least one hour (e.g. 1-200 hours) at a pressure of 100-2,500 kPa. In a more particular embodiment, the catalyst can be made to undergo steaming with 75-100% steam at 315-500°C and atmospheric pressure for 2-25 hours.

The invention will now be more particularly described with reference to the following Examples and the accompanying drawings in which :

Fig. 1 graphically shows C_7^+ aromatics HDA conversion for Pt/MCM-22 compared with thermal HDA;

Fig. 2 graphically shows benzene HDA selectivity over a range of C_7^+ conversions for Pt/MCM-22 compared with thermal HDA;

Fig. 3 graphically shows C_9^+ aromatics HDA conversion for Pt/MCM-22 compared with thermal HDA; and,

Fig. 4 graphically shows BTX HDA selectivity over a range of C_9^+ conversions for Pt/MCM-22 compared with thermal HDA.

In examples illustrative of the synthesis of zeolite, whenever sorption data are set forth for comparison of sorptive capacities for water, cyclohexane and/or n-hexane, they were Equilibrium Adsorption values determined as follows:

A weighed sample of the calcined adsorbent was contacted with the desired pure adsorbate vapor in an adsorption chamber, evacuated to less than 1 mm Hg and contacted with 12 Torr of water vapor or 40 Torr of n-hexane or 40 Torr of cyclohexane vapor, pressures less than the vapor-liquid equilibrium pressure of the respective adsorbate at 90°C. The pressure was kept constant (within about ± 0.5 mm Hg) by addition of adsorbate vapor controlled by a manostat during the adsorption period, which did not exceed about 8 hours. As adsorbate was adsorbed by the crystalline material, the decrease in pressure caused the manostat to open a valve which admitted more adsorbate vapor to the chamber to restore the above control pressures. Sorption was complete when the pressure change was not sufficient to activate the manostat. The increase in weight was calculated as the adsorption capacity of the sample g/100 g of calcined adsorbant. Zeolite MCM-22 always exhibits Equilibrium Adsorption values of

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greater than about 10 wt.% for water vapor, greater than about 4.5 wt.%, usually greater than about 7 wt.% cyclohexane vapor and greater than about 10 wt.% for n-hexane vapor. These vapor sorption capacities are a notable distinguishing feature of zeolite MCM-22.

When Alpha Value is examined, it is noted that the Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst taken as an Alpha of 1 (Rate Constant = 0.016 sec^{-1}). The Alpha Test is described in U.S. Patent No. 3,354,078; in the Journal of Catalysis, vol. 4, p. 527 (1965); vol. 6, p. 278 (1966); and vol. 61, p. 395 (1980). The experimental conditions of the test used herein include a constant temperature of 538°C and a variable flow rate as described in detail in the Journal of Catalysis, vol. 61, p. 395.

EXAMPLE 1

One part sodium aluminate (43.5% Al_2O_3 , 32.2% Na_2O , 25.6% H_2O) was dissolved in a solution containing 1 part of 50% NaOH solution and 103.13 parts H_2O . To this were added 4.50 parts hexamethyleneimine. The resulting solution was added to 8.55 parts of UltrasilTM, a precipitated, spray-dried silica (90% SiO_2).

The reaction mixture had the following composition in mole ratios:

30	$\text{SiO}_2/\text{Al}_2\text{O}_3$	=	30.0
	OH^-/SiO_2	=	0.18
	$\text{H}_2\text{O}/\text{SiO}_2$	=	44.9
	Na/SiO_2	=	0.18
	R/SiO_2	=	0.35

35 where R is hexamethyleneimine.

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The mixture was crystallized in a stainless steel reactor, with stirring, at 150°C for 7 days. The resultant MCM-22 crystalline product was filtered, washed with water and dried at 120°C. After a 20 hour calcination at 538°C, the X-ray diffraction pattern contained the major lines listed in Table E. The sorption capacities of the calcined material were measured to be:

H ₂ O	15.2 wt.%
Cyclohexane	14.6 wt.%
n-Hexane	16.7 wt.%

The surface area of the zeolite was measured to be 494 m₂/g.

The chemical composition of the uncalcined material was determined to be as follows:

<u>Component</u>	<u>wt.%</u>
SiO ₂	66.9
Al ₂ O ₃	5.40
Na	0.03
N	2.27
Ash	76.3
SiO ₂ O/Al ₂ O ₃ , mole ratio	21.10

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TABLE E

	Degrees <u>2-Theta</u>	Interplanar <u>d-Spacing (A)</u>	<u>I/I^o</u>
	2.80	31.55	25
5	4.02	21.98	10
	7.10	12.45	96
	7.95	11.12	47
	10.00	8.85	51
	12.90	6.86	11
10	14.34	6.18	42
	14.72	6.02	15
	15.90	5.57	20
	17.81	4.98	5
	20.20	4.40	20
15	20.91	4.25	5
	21.59	4.12	20
	21.92	4.06	13
	22.67	3.92	30
	23.70	3.75	13
20	24.97	3.57	15
	25.01	3.56	20
	26.00	3.43	100
	26.69	3.31	14
	27.75	3.21	15
25	28.52	3.13	10
	29.01	3.08	5
	29.71	3.01	5
	31.61	2.830	5
	32.21	2.779	5
30	33.35	2.687	5
	34.61	2.592	5

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EXAMPLE 2

A portion of the calcined crystalline product of Example 1 was tested in the Alpha Test and was found to have an Alpha Value of 224.

EXAMPLES 3-5

5 Three separate synthesis reaction mixtures were prepared with compositions indicated in Table F. The mixtures were prepared with sodium aluminate, sodium hydroxide, UltrasilTM, hexamethyleneimine (R) and water. The mixtures were maintained at 150°C, 143°C and 150°C, 10 respectively, for 7, 8 and 6 days respectively in stainless steel autoclaves at autogenous pressure. Solids were separated from any unreacted components by filtration and then water washed, followed by drying at 120°C. The product crystals were subjected to X-ray 15 diffraction, sorption, surface area and chemical analyses. The results of the sorption, surface area and chemical analyses are presented in Table F. The sorption and surface area measurements were of the calcined product.

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TABLE F

<u>Example</u>		<u>3</u>	<u>4</u>	<u>5</u>
Synthesis Mixture, mole ratios				
5	SiO ₂ /Al ₂ O ₃	30.0	30.0	30.0
	OH ⁻ /SiO ₂	0.18	0.18	0.18
	H ₂ O/SiO ₂	19.4	19.4	44.9
	Na/SiO ₂	0.18	0.18	0.18
	R/SiO ₂	0.35	0.35	0.35
Product Composition, Wt.%				
10	SiO ₂	64.3	68.5	74.5
	Al ₂ O ₃	4.85	5.58	4.87
	Na	0.08	0.05	0.01
	N	2.40	2.33	2.12
	Ash	77.1	77.3	78.2
15	SiO ₂ O/Al ₂ O ₃ , mole ratio	22.5	20.9	26.0
<u>Adsorption, Wt.%</u>				
H ₂ O		14.9	13.6	14.6
Cyclohexane		12.5	12.2	13.6
n-Hexane		14.6	16.2	19.0
20	Surface Area, m ² /g	481	492	487

EXAMPLE 6

Quantities of the calcined (538^oC for 3 hours) crystalline silicate products of Examples 3, 4 and 5 were tested in the Alpha Test and found to have Alpha Values of 227, 180 and 187, respectively.

EXAMPLE 7

To demonstrate a further preparation of the present zeolite, 4.49 parts of hexamethyleneimine were added to a solution containing 1 part of sodium aluminate, 1 part of 50% NaOH solution and 44.19 parts of H₂O. To the combined solution was added 8.54 parts

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of Ultrasil silica. The mixture were crystallized with agitation at 145°C for 59 hours and the resultant product was water washed and dried at 120°C.

Product chemical composition, surface area and adsorption analyses results were as set forth in Table G:

TABLE G

Product Composition (uncalcined)

	C	12.1 wt.%
10	N	1.98 wt.%
	Na	640 ppm
	Al ₂ O ₃	5.0 wt.%
	SiO ₂	74.9 wt.%
	SiO ₂ /Al ₂ O ₃ , mole ratio	25.4
15	Adsorption, wt.%	
	Cyclohexane	9.1
	n-Hexane	14.9
	H ₂ O	16.8
	Surface Area, m ² /g	479

20

EXAMPLE 8

This example illustrates the preparation of zeolite MCM-22 where X in the general formula, supra, is boron. Boric acid, 2.59 parts, was added to a solution containing 1 part of 45% KOH solution and 42.96 parts H₂O. To this was added 8.56 parts of UltrasilTM silica, and the mixture was thoroughly homogenized. A 3.88 parts quantity of hexamethyleneimine was added to the mixture.

The reaction mixture had the following composition in mole ratios:

$\text{SiO}_2/\text{B}_2\text{O}_3$	=	6.1
OH^-/SiO_2	=	0.06
$\text{H}_2\text{O}/\text{SiO}_2$	=	19.0
K/SiO_2	=	0.06
R/SiO_2	=	0.30

where R is hexamethyleneimine.

The mixture was crystallized in a stainless steel reactor, with agitation, at 150°C for 8 days. The crystalline product was filtered, washed with water and dried at 120°C . A portion of the product was calcined for 6 hours at 240°C and found to have the following sorption capacities:

H_2O	11.7 wt. %
Cyclohexane	7.5 wt. %
n-Hexane	11.4 wt. %

The surface area of the calcined crystalline material was measured (BET) to be $405 \text{ m}^2/\text{g}$.

The chemical composition of the uncalcined material was determined to be as follows:

N	1.94 wt. %
Na	175 ppm
K	0.60 wt. %
Boron	1.04 wt. %
Al_2O_3	920 ppm
SiO_2	75.9 wt. %
Ash	74.11 wt. %
$\text{SiO}_2/\text{Al}_2\text{O}_3$, molar ratio	1406
$\text{SiO}_2/(\text{Al}+\text{B})_2\text{O}_3$, molar ratio	25.8

EXAMPLE 9

A sample of platinum exchanged MCM-22 catalyst was prepared from the zeolite produced in Example 1. The zeolite was initially exchanged with ammonium nitrate and then mixed with an aluminum oxide binder. The mixture was milled, extruded and dried at 120°C (250°F), whereafter the mixture was calcined in nitrogen at 540°C (1000°F) for 3 hours. After humidification the mixture was exchanged with 1 N ammonium nitrate, dried and calcined again in nitrogen at 540°C (1000°F). The mixture was again humidified, exchanged with Pt(NH₃)₄Cl₂ solution for 8 hours, rinsed, dried and calcined at 350°C (660°F) in air. This catalyst had the properties shown in Table H.

Table HProperties of Pt/MCM-22 CatalystComposition, wt%

Zeolite*	65
Platinum	0.66
Alumina*	35

Density, g/cc

Packed	0.45
Particle	0.73
Real	2.60

Physical Properties

Pore Volume, cc/g	0.99
Surface Area, m ² /g	372
Avg. Pore Diameter, Å	81

*Prior to platinum addition

EXAMPLE 10

A feed containing 96.8 mole % C_9^+ aromatics and added hydrogen was contacted with the Pt/MCM-22 catalyst of Example 9. The reaction conditions included a pressure of 1480 kPa (200 psig), 2.5 LHSV, and 360 Nm^3/m^3 (2000 scf/bbl) hydrogen. The temperature was varied between 315 and 480°C (600 and 900°F). The resulting product yields in moles are tabulated in Table I. Conversions and selectivities are calculated in accordance with the following formulae:

(1) Based on 100 moles of feed, the C_7^+ mono-aromatics conversion is defined as:

$$C_7^+ \text{ conversion} = 100 \times \frac{(\text{moles of } C_7^+)_{\text{feed}} - (\text{moles of } C_7^+)_{\text{product}}}{(\text{moles of } C_7^+)_{\text{feed}}}$$

where C_7^+ are mono-aromatics including $C_7 \dots C_{12}$ mono-aromatics. Diaromatics (naphthalene and its alkyl derivatives) are not included in C_7^+ .

(2) The benzene selectivity is defined as:

$$\text{Benzene selectivity} = 100 \times \frac{(\text{moles of benzene})_{\text{product}} - (\text{moles of benzene})_{\text{feed}}}{(\text{moles of } C_7^+)_{\text{feed}} - (\text{moles of } C_7^+)_{\text{product}}}$$

(3) Similarly, the C_9^+ conversion and BTX selectivity are defined as:

$$C_9^+ \text{ conversion} = 100 \times \frac{(\text{moles of } C_9^+)_{\text{feed}} - (\text{moles of } C_9^+)_{\text{product}}}{(\text{moles of } C_9^+)_{\text{feed}}}$$

$$\text{BTX selectivity} = 100 \times \frac{(\text{moles of BTX})_{\text{product}} - (\text{moles of BTX})_{\text{feed}}}{(\text{moles of } C_9^+)_{\text{feed}} - (\text{moles of } C_9^+)_{\text{product}}}$$

Table I
Pt MCM-22 Hydrodealkylation of C₉+ Aromatics

Conditions		Feed		Products					
Temp., °F °C		600	700	750	800	825	850	900	
5		315	370	400	427	440	454	480	
10									
Yields, moles									
C ₁		-	0.2	0.8	2.2	3.3	4.7	6.9	
C ₂		0.4	7.5	19.4	42.9	57.7	69.2	69.0	
C ₃		11.1	26.4	27.2	27.1	25.9	28.7	26.0	
C ₄		5.4	9.3	7.4	8.6	8.4	7.5	6.0	
C ₅		2.2	4.0	2.2	4.6	4.0	1.6	1.0	
C ₆ + Saturates		1.6	3.0	0.7	0.5	0.6	0.6	0.6	
Diaromatics		3.8	3.9	5.0	4.8	5.5	5.8	6.0	
C ₆ , Benzene		16.0	31.6	33.8	39.1	39.9	45.5	45.8	
C ₇ , Toluene		5.8	2.7	3.7	6.0	7.8	15.1	15.4	
C ₈ , Xylene		7.8	21.4	24.1	19.5	15.5	8.8	9.0	
C ₉ , Aromatics		15.8	3.4	4.4	4.0	4.3	3.7	3.7	
C ₁₀ , Aromatics		39.3	24.3	16.5	15.5	12.5	8.3	8.5	
C ₁₁ , Aromatics		3.5	1.3	0.6	0.3	0.3	0.9	0.9	
C ₁₂ , Aromatics		2.1	2.7	2.7	1.7	1.6	0.9	0.9	
C ₁₃ , Aromatics		0.1	0.1	0.1	0	0.1	0	0	
H ₂ Consum., scf/bbl		144	370	379	660	796	897	864	
Nm ³ /m		26	66	67	117	142	160	154	
For Benzene Production									
C ₇ + Conversion, %		19.0	39.5	44.0	49.4	54.4	59.3	58.1	
Selectivity, %		67.0	74.8	73.7	76.8	70.8	75.5	78.0	
For BTX Production									
C ₉ + Conversion, %		21.0	59.0	68.6	72.3	75.7	82.2	82.0	
Selectivity, %		63.8	79.7	79.5	80.9	74.8	78.9	79.8	

5

10

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EXAMPLE 11

A thermal hydrodealkylation run was conducted with a feedstock of the same composition as that of Example 10. The reactor contained quartz chips in place of the Pt/MCM-22, and the reaction was conducted at 1480 kPa (200 psig), 2.5 LHSV, 890 Nm³/m³ (5000 scf/bbl) H₂ at temperatures of 427°C and 454°C (800°F and 850°F).

The resulting product mole yields, conversion and selectivities are tabulated in Table J.

Table J

Thermal Hydrodealkylation of C₉⁺ Aromatics

Conditions	Feed	Product	
Temperature, °F		800	850
°C		427	454
Yields, moles			
C ₂		0.5	0.1
C ₃		0.6	0.1
C ₄		0.1	3.2
C ₅ ⁺	0.2	0.2	0.3
C ₆ Saturates	3.0	3.4	3.5
Diaromatics	3.0	3.4	3.5
C ₆ , Benzene	4.2	4.9	4.8
C ₇ , Toluene	9.2	9.6	9.6
C ₈ , Xylene	5.8	6.6	9.6
C ₉ Aromatics	27.8	26.7	26.9
C ₁₀ Aromatics	44.8	43.2	43.2
C ₁₁ Aromatics	4.0	3.8	3.8
C ₁₂ Aromatics	1.0	.9	1.0
H ₂ Consumption,			
scf/bbl		19	85
Nm ³ /m ³		3.4	15
For Benzene Production			
C ₇ ⁺ Conversion, %		1.9	1.9
Selectivity		36.8	33.0
For BTX Production			
C ₉ ⁺ Conversion, %		3.9	3.5
Selectivity		63	55.5

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EXAMPLE 12

Hydrodealkylation conversion of a heavy gasoline made by the LCO upgrading process was conducted with the Pt/MCM-22 catalyst of Example 9. The reaction conditions include an LHSV of 2.5 hr^{-1} , a pressure of 1480 kPa (200 psig), a hydrogen feed rate of $360 \text{ Nm}^3/\text{m}^3$ (2000 scf/bbl), and temperatures of 454°C and 480°C (850°F and 900°F).

Table K presents a tabulation of the composition of the feed and the products as well as reaction conditions, conversion and selectivity.

Table K
Pt MCM-22 Hydrodealkylation of Heavy Gasoline

	<u>Conditions</u>		<u>Feed</u>	<u>Products</u>	
	Temperature, °F	°C		850	900
5				454	480
<u>Yields, moles</u>					
	C ₁			3.5	7.7
	C ₂			19.2	29.0
	C ₃			21.6	23.9
10	C ₄			10.6	4.5
	C ₅			5.2	1.1
	C ₆ + Saturates	26.8		19.5	14.8
	Diaromatics	8.7		4.5	5.8
	C ₆ , Benzene	3.0		10.7	9.0
15	C ₇ , Toluene	14.8		21.9	22.6
	C ₈ , Xylene	20.2		17.2	17.1
	C ₉ Aromatics	14.1		8.4	9.0
	C ₁₀ Aromatics	7.4		3.6	4.2
	C ₁₁ Aromatics	4.8		1.5	1.9
20	C ₁₂ Aromatics	0.2		0.1	0.1
	H ₂ Consumption, scf/bbl			440	640
	Nm ³ /m ³			78	114
<u>For Benzene Production</u>					
	C ₇ + Conversion, %			14.3	10.7
25	Selectivity			87.5	90.9
<u>For BTX Production</u>					
	C ₉ + Conversion, %			71.7	66.5
	Selectivity			34.3	33.3

Fig. 1 is a graph showing C_7+ aromatics conversion % for the hydrodealkylation reaction of the present invention using Pt/MCM-22 catalyst as opposed to the conversion for the thermal dealkylation method over a temperature range of 315 to 480°C (600 to 900°F). Data for this graph is extracted from Tables I and J, infra, as pertaining to benzene production.

Fig. 2 is a graph showing the benzene selectivity for the hydrodealkylation reaction of the present invention using Pt/MCM-22 catalyst, in comparison with the benzene selectivity of the thermal dealkylation method, over a range of C_7+ aromatics conversion. The data for this graph is extracted from Tables I and J, infra, as pertaining to benzene production.

Fig. 3 is a graph showing C_9+ aromatics conversion of the hydrodealkylation reaction of the present invention using Pt/MCM-22 catalyst in comparison with the conversion of the thermal dealkylation method over a temperature range of 315 to 480°C (600°F to 900°F). The data for this graph is extracted from Tables I and J, infra, as pertaining to BTX production.

Fig. 4 is a graph showing the BTX selectivity for the hydrodealkylation reaction of the present invention using Pt/MCM-22 catalyst in comparison with the BTX selectivity for the thermal dealkylation method, over a range of C_9+ aromatics conversion. The data for this graph is extracted from Tables I and J, infra, as pertaining to BTX production.

The above-mentioned tables and graphs clearly illustrate that the process of the invention is much more active and selective than thermal hydrodealkylation for benzene production from heavy aromatics. For example, at 454°C (850°F), the catalyst of the invention achieved 59.3% conversion of C_7+ aromatics and gave a benzene selectivity of 75.5 mole %

(Example 10). At the same conditions, the thermal hydrodealkylation achieved only 1.9% conversion with a benzene selectivity of 33 mole %. Similar conclusions are applied to the BTX production, in which conversion is defined as conversion of C_9+ aromatics.

The C_9+ aromatics feed used in Example 10 had a total aromatics purity of 96.8 mole %. This high aromatics purity is desirable because it simplifies product separation and purification. However, to maximize process flexibility, it is also desirable to have a process that can handle a wide range of feed compositions. The feed flexibility of the process of the invention is demonstrated by Example 12, in which the feed was a C_6+ gasoline produced from an LCO upgrading process and contained 64.5 mole % C_6-C_{12} aromatics, 26.8 mole % saturates, and 8.7 mole % diaromatics. The results in Table K show that the present catalyst maintained its effectiveness for processing feeds with lower concentration of aromatics. For example, at 850°F and 2.5 LHSV, processing with the present catalyst increased the benzene content of the C_6+ gasoline from 3.0% to 10.7% moles based on feed. Similarly, the overall BTX concentration increased from 38 moles to 49.8 moles.

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CLAIMS:

1. A process for catalytic hydrodealkylation of a hydrocarbon feedstock containing alkylaromatic compounds to provide a hydrodealkylated product containing benzene, said process comprising contacting said feedstock with a catalyst composition comprising nickel or a noble metal and a synthetic zeolite characterized by an X-ray diffraction pattern including values set forth below in Table A:

TABLE A

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
12.36 $\pm$ 0.4	M-VS
11.03 $\pm$ 0.2	M-S
8.83 $\pm$ 0.14	M-VS
6.18 $\pm$ 0.12	M-VS
6.00 $\pm$ 0.10	M-M
4.06 $\pm$ 0.07	W-S
3.91 $\pm$ 0.07	M-VS
3.42 $\pm$ 0.06	VS

2. The process of Claim 1 wherein said zeolite is characterized by an X-ray diffraction pattern including values set forth below in Table B:

TABLE B

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, $I/I_0 \times 100$</u>
30.0 $\pm$ 2.2	W-M
22.1 $\pm$ 1.3	W
12.36 $\pm$ 0.4	M-VS
11.03 $\pm$ 0.2	M-S
8.83 $\pm$ 0.14	M-VS
6.18 $\pm$ 0.12	M-VS
6.00 $\pm$ 0.10	W-M
4.06 $\pm$ 0.07	W-S
3.91 $\pm$ 0.07	M-VS
3.42 $\pm$ 0.06	VS

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3. The process of Claim 1 wherein the zeolite is characterized by an X-ray diffraction pattern including values set forth below in Table C:

TABLE C

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.86 ± 0.14	W-M
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
5.54 ± 0.10	W-M
4.92 ± 0.09	W
4.64 ± 0.08	W
4.41 ± 0.08	W-M
4.25 ± 0.08	W
4.10 ± 0.07	W-S
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.75 ± 0.06	W-M
3.56 ± 0.06	W-M
3.42 ± 0.06	VS
3.30 ± 0.05	W-M
3.20 ± 0.05	W-M
3.14 ± 0.05	W-M
3.07 ± 0.05	W
2.99 ± 0.05	W
2.82 ± 0.05	W
2.78 ± 0.05	W
2.68 ± 0.05	W
2.59 ± 0.05	W

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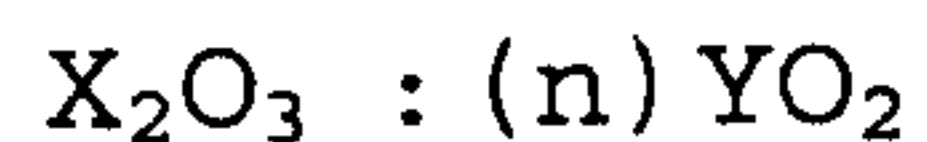
4. The process of Claim 1 wherein the zeolite is characterized by an X-ray diffraction pattern including values set forth below in Table D:

TABLE D

<u>Interplanar d-Spacing (A)</u>	<u>Relative Intensity, I/I₀ x 100</u>
30.0 ± 2.2	W-M
22.1 ± 1.3	W
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.86 ± 0.14	W-M
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
5.54 ± 0.10	W-M
4.92 ± 0.09	W
4.64 ± 0.08	W
4.41 ± 0.08	W-M
4.25 ± 0.08	W
4.10 ± 0.07	W-S
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.75 ± 0.06	W-M
3.56 ± 0.06	W-M
3.42 ± 0.06	VS
3.30 ± 0.05	W-M
3.20 ± 0.05	W-M
3.14 ± 0.05	W-M
3.07 ± 0.05	W
2.99 ± 0.05	W
2.82 ± 0.05	W
2.78 ± 0.05	W
2.68 ± 0.05	W
2.59 ± 0.05	W

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5. The process of any one of the preceding Claims wherein the synthetic zeolite has a composition comprising the molar relationship:



wherein X is a trivalent element selected from the group consisting of aluminum, boron, iron and gallium, Y is a tetravalent element selected from the group consisting of silicon and germanium, and n is at least 10.

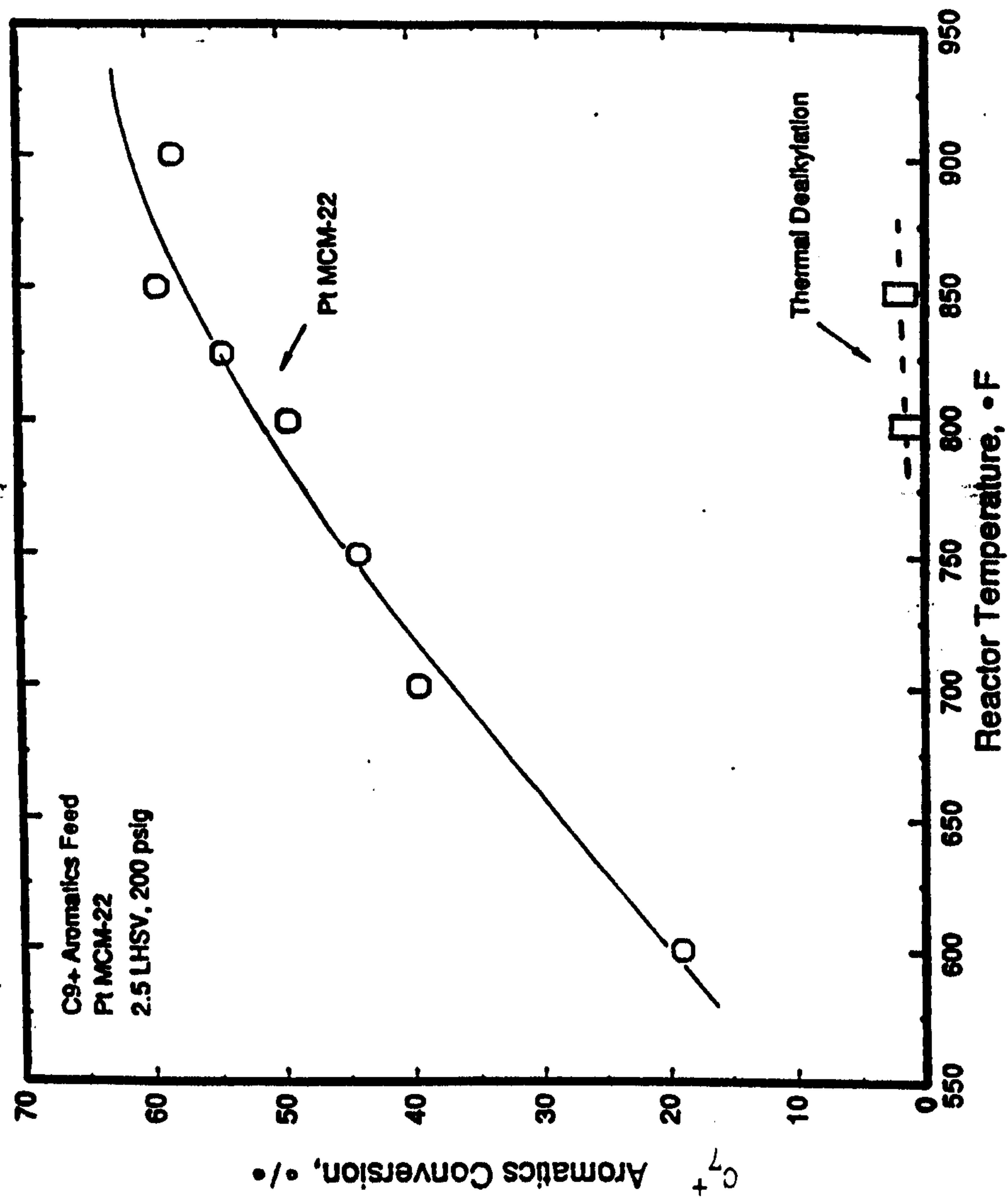
6. The process of any one of the preceding Claims wherein said noble metal is platinum or palladium.

7. The process of any one of the preceding Claims wherein said feedstock comprises more than 50 mole % C₆-C₁₂ single-ring aromatics.

8. The process of any one of the preceding Claims wherein said feedstock comprises more than 50 mole % C₉-C₁₂ single-ring aromatics.

9. The process of any one of the preceding Claims wherein said contacting is effected at a temperature of 315 to 540° (600 to 1000°F), a pressure of 445 to 3550 kPa (50 to 500 psig), a hydrogen circulation rate of 89 to 890 Nm³/m³ (500 to 5000 scf/bbl), and a liquid hourly space velocity of 0.5 to 10 hr⁻¹.

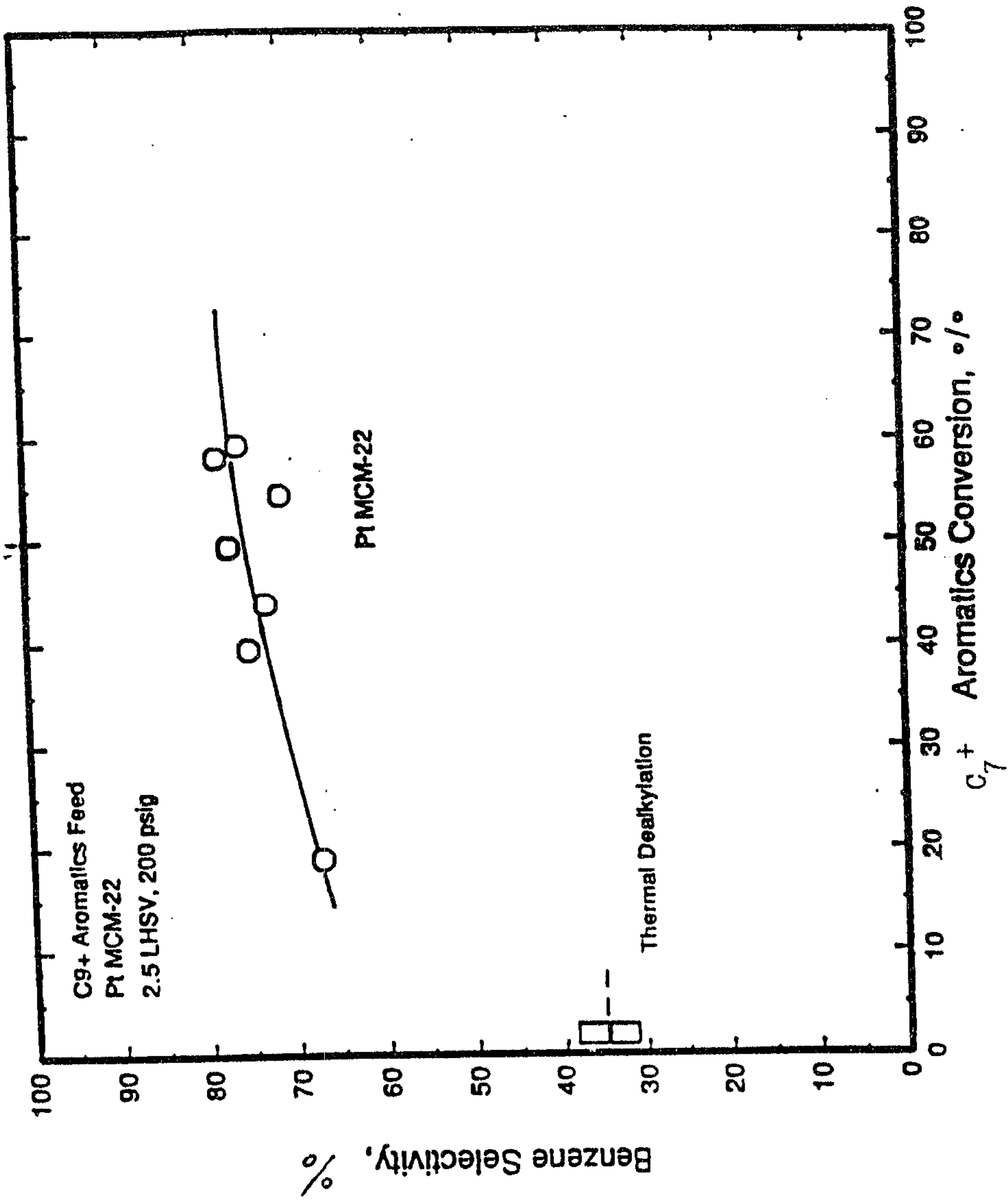
FIG. 1



Kirby, Eades, Gale
Baker & Potvin

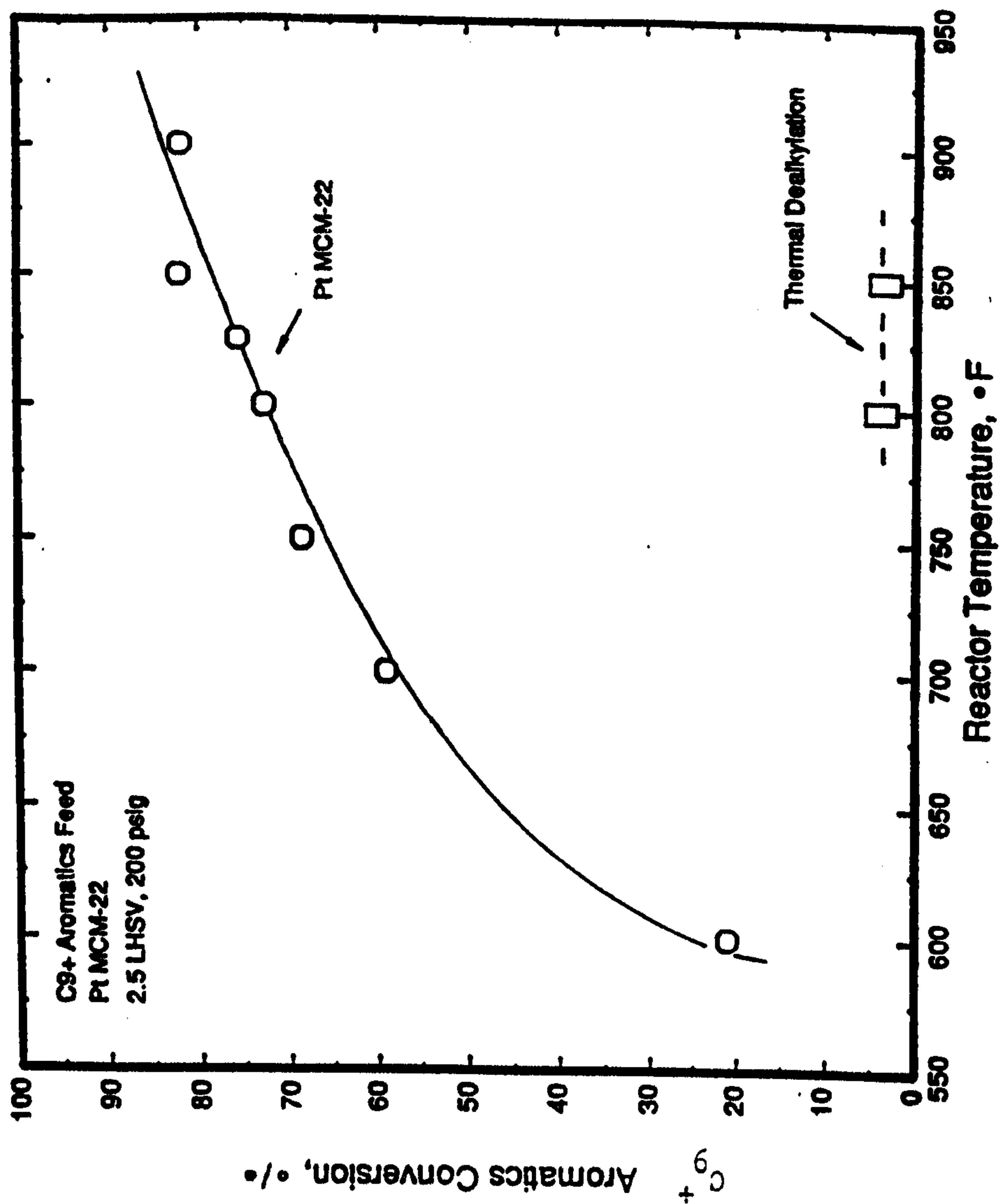
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FIG 2



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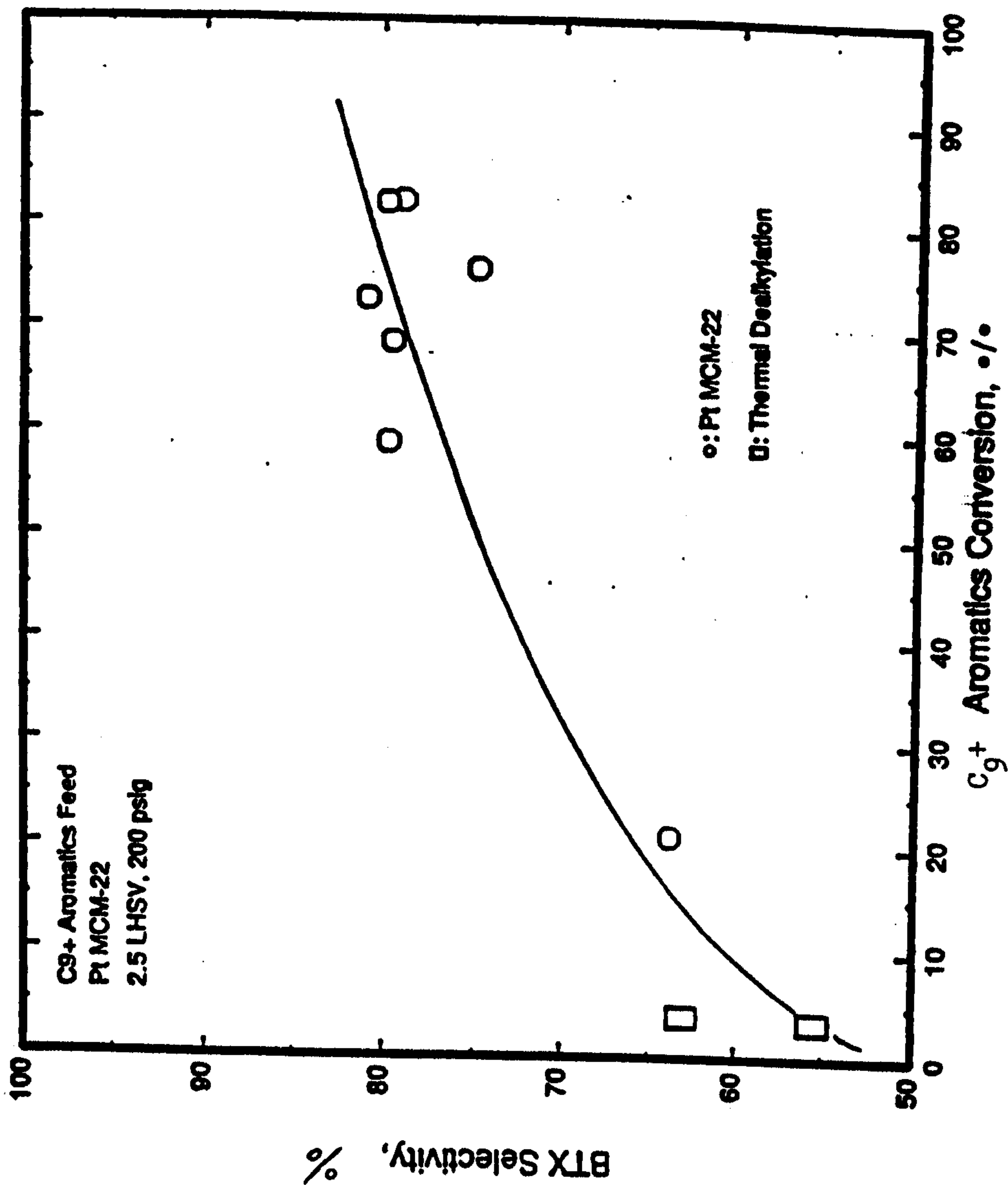
FIG 3



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Kirby, Eades, Gale
 Baker & Butcher

Fig 4



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Wiley, Ludes, Gale
 Baker & Potts