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(54) Title: PARAFFIN ISOMERIZATION PROCESS

(57) Abstract

Paraffins, especially light paraffins in the C_4-C_8 range, are isomerized to iso-paraffins over an isomerization catalyst comprising a noble metal such as platinum on a support material comprising an inorganic, non-layered, porous, crystalline phase aluminosilicate material which exhibits, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than 18 Å and a benzene adsorption capacity greater than about 15 grams benzene per 100 grams at 50 torr and 25 °C. In its preferred form, the support material has a uniform, hexagonal arrangement of pores with diameters of at least about 13 Å and a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than about 18 Å which corresponds to at least one peak in the X-ray diffraction pattern.

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PARAFFIN ISOMERIZATION PROCESS

This invention relates to a process for isomerizing paraffins, especially light paraffins in the C_4-C_8 range to produce branched chain paraffins.

The isomerization of paraffins, especially light paraffins, is an established refining process which is traditionally used to provide additional feedstock for alkylation units or to convert relatively low octane linear paraffins to higher octane, branched chain isomers which can be blended into the gasoline pool. Straight chain paraffins such as n-butane, n-pentane and n-hexane are converted to the corresponding isoparaffins by various isomerization processes which may use various types of catalysts.

Existing processes for isomerizing paraffins employ non-regenerable Lewis and Bronsted acid catalysts, for example, as disclosed in U.S. Patents Nos. 3,766,286; 3,852,184; 3,855,346; 3,839,489; 4,144,282 and 4,814,544. Commercial processes of this type have been developed by various companies including Phillips Petroleum Company and Shell Development Company.

An alternative type of catalyst used in a number of commercial isomerization processes comprises a metal hydrogenation/dehydrogenation component, usually platinum, on a porous support. An example of this process is the Penex process (UOP) in which the isomerization is carried out in the presence of hydrogen and a platinum catalyst. The Iso-Kel process (M.W. Kellogg) also employs a precious metal catalyst with hydrogen circulation and the Pentafining (Arco/Englehardt) and Butamer (UOP) processes also employ platinum on supports with external hydrogen circulation. Processes of this kind are disclosed, for example, in U.S. Patents Nos. 4,834,866 and 4,783,575.

Isomerization processes utilizing metal components on supports comprising a molecular sieve are disclosed in U.S. Patents Nos. 3,842,114 (Sie); 3,836,597 (Sie); 4,778,944 (Zarchy) and 4,374,296 (Haag).

Paraffin isomerization catalysts may also be employed as ring opening catalysts for the removal of cyclic aromatic precursors from reformer feedstocks as disclosed in U.S. 4,783,575 and U.S. 4,834,866. For example, cyclohexane, a precursor of benzene, may be isomerized to a mixture of branched paraffins which are only partly aromatized in the reformer so as to minimize the production of benzene. The utilization of paraffin isomerization for ring opening aromatic precursors, especially cyclohexane, is likely to become more important in the future as environmental regulations limit the aromatic content of motor gasoline.

It has now been found that a class of novel, porous materials may be used as the basis for catalysts which are useful for the isomerization of linear low molecular weight paraffins to form branched-chain isoparaffins of higher octane rating. The isomerization catalysts based on these novel, porous materials have been found to produce significantly less cracked products than other metal containing catalysts such as platinum on silica-alumina.

Accordingly the present invention resides in a process for isomerizing paraffins comprising contacting a paraffin feed with an isomerization catalyst comprising a hydrogenation/dehydrogenation component on a porous support which includes an inorganic, porous, non-layered crystalline phase material exhibiting, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Angstrom Units with a relative intensity of 100 and having a benzene adsorption capacity of greater than 15 grams of benzene per 100 grams of said material at 6.7 kPa (50 torr) and 25°C.

A Lewis acid or Bronsted acid may also be incorporated into the porous material as an additional isomerization promoter.

Preferably, the crystalline phase is material is characterized by a microstructure with a uniform, hexagonal arrangement of pores with diameters of at least about 13 Å which, after calcination, exhibits an X-ray diffraction pattern with at least one d-spacing greater than about 18 Å with a relative intensity of 100 and a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than about 18 Å which corresponds to at least one peak in the X-ray diffraction pattern. Such a material is identified herein as MCM-41 and is usually synthesized as a metallosilicate with Bronsted acid sites by incorporating a tetrahedrally coordinated trivalent element such as Al, Ga, B, or Fe within the silicate framework. The preferred catalytic form is the aluminosilicate although other forms such as the boroaluminosilicate may also be used.

The present process may be used to isomerize C_4-C_8 paraffin hydrocarbons, either as pure compounds or mixtures. In refinery operation, the paraffins will normally be present in mixtures and in addition to the C_4-C_8 materials, may contain hydrocarbons boiling outside this range; cycloparaffins and aromatics may also be present. Thus, the feed will comprise C_4-C_8 paraffins such as butane, pentane, hexane and these may be present in refinery streams such as raffinate cuts from solvent extraction units, reformer feedstock or pyrolysis gasoline from ethylene crackers. The feeds may also contain cyclic hydrocarbons, e.g. in the form of C_6+ naphthas; the cyclic materials in such feeds may undergo ring opening reactions in the presence of the catalyst with its associated metal component, to form paraffins which then undergo isomerization to iso-paraffins which can be separated from the cyclics by fractionation with the cyclics being recycled to extinction.

Reaction temperatures are suitably in the range 200°-800°F (93 to 425°C); temperatures outside this range may be utilized although they are normally less preferred; temperatures from 400 to 700°F (205 to 370°F) are typical. Pressures will normally be up to about 1000 psig (7,000 kPa abs.) although there is no reason why higher pressures should not be utilized. Lower pressures, in the range of 50 to 100 psig (445 to 790 kPa abs.) may readily be employed and the use of relatively low pressures within this range will generally be preferred in order to permit the use of low pressure equipment. The isomerization is usually carried out in the presence of hydrogen, typically at a molar ratio relative to the feed from 0.1 to 10:1 and usually from 0.5:1 to 2:1. Space velocities are typically from 0.1 to 10 WHSV and usually from 0.5 to 5 WHSV. When an additional acidic material (Lewis acid or Bronsted acid) is included in the catalyst, lower operational temperatures may be used, favoring the isomerization over the less desired cracking reactions.

The catalyst used in the present isomerization process comprises a metal component on a support of relatively low acidity which provides the desired degree of acidic functionality for the isomerization reactions while minimizing conversion to cracked products boiling outside the desired boiling range during the operation.

A metal component of the catalyst is included in order to promote the desired isomerization reactions which, proceeding through unsaturated transitional species, require mediation by a hydrogenation-dehydrogenation component. In order to maximize the isomerization activity of the catalyst, metals having a strong hydrogenation function are preferred and for this reason, platinum and the other noble metals such as palladium, rhodium, iridium, rhenium are given a preference although other metals capable of acting as a hydrogenation component may also be used, for example, nickel, tungsten or other metals of Group VIIIA of the Periodic Table (IUPAC Table), either singly, in mixtures or in combination with other metals. The amount of the noble metal hydrogenation component is typically in the range 0.1 to 5 weight percent of the total catalyst, usually from 0.1 to 2 weight percent. Base metal hydrogenation components may be added usually in somewhat greater amounts. The hydrogenation component can be exchanged onto the support material, impregnated into it or physically admixed with it. If the metal is to be impregnated into or exchanged onto the mesoporous support, it may be done, for example, by treating the support with a platinum metal-containing ion. Suitable platinum compounds include chloroplatinic acid, platinous chloride and various compounds containing the platinum ammine complex. The metal compounds may be either compounds in which the metal is present in the cation or anion of the compound. Platinum compounds in which the metal is in the form of a cation or cationic complex, e.g., $Pt(NH_3)_4Cl_2$ are particularly useful, as are anionic complexes such as the vanadate and metatungstate ions.

The catalyst may be subjected to a final calcination under conventional conditions in order to convert the metal component to the oxide form and to confer the required mechanical strength on the catalyst. Prior to use the catalyst may be subjected to presulfiding.

Higher isomerization activity may be provided by the inclusion of a material having Lewis or Bronsted acid activity in the catalyst. For this purpose, both liquid and solid acid materials may be used: the high surface area of the mesoporous materials enables significant amounts of the added acidic material to be taken up. Examples of suitable additional acidic materials include aluminum trichloride, boron trifluoride and complexes of boron trifluoride, for example, with water, lower alcohols or esters. The maximum amount which may added is set by the ability of the support material to sorb the added component and is readily determined by experiment. The use of the added acidic material is desirable since it enables the reaction conditions to be optimized for the production of the iso-paraffinic product while minimizing the cracking to lower boiling products.

The support material used for the catalyst is a mesoporous crystalline material which is described in detail below. When it is used in the present catalysts, the mesoporous crystalline material is at least partly in the decationized or hydrogen form in order to provide the desired degree of acidic functionality for the isomerization reactions.

The support material used in the present catalyst includes an inorganic, porous, non-layered crystalline phase material which can be characterized (in its calcined form) by an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Å (4.909 degrees two-theta for Cu K-alpha radiation) with a relative intensity of 100 and a benzene sorption capacity of greater than 15 grams of benzene per 100 grams of the the material at 50 torr and 25°C. More particularly, the calcined crystalline non-layered material of the invention may be characterized by an X-ray diffraction pattern with at least two peaks at positions greater than about 10 Angstrom Units d-spacing (8.842 degrees two-theta for Cu K-alpha radiation), at least one of which is at a position greater than about 18 Angstrom Units d-spacing, and no peaks at positions less than about 10 Angstrom units d-spacing with relative intensity greater than about 20% of the strongest peak. Still more particularly, the

X-ray diffraction pattern of the calcined material of this invention will have no peaks at positions less than about 10 Angstrom units d-spacing with relative intensity greater than about 10% of the strongest peak.

X-ray diffraction data were collected on a Scintag PAD X automated diffraction system employing theta-theta geometry, Cu K-alpha radiation, and an energy dispersive X-ray detector. Use of the energy dispersive X-ray detector eliminated the need for incident or diffracted beam monochromators. Both the incident and diffracted X-ray beams were collimated by double slit incident and diffracted collimation systems. The slit sizes used, starting from the X-ray tube source, were 0.5, 1.0, 0.3 and 0.2 mm, respectively. Different slit systems may produce differing intensities for the peaks. The materials of the present invention that have the largest pore sizes may require more highly collimated incident X-ray beams in order to resolve the low angle peak from the transmitted incident X-ray beam.

The diffraction data were recorded by step-scanning at 0.04 degrees of two-theta, where theta is the Bragg angle, and a counting time of 10 seconds for each step. The interplanar spacings, d's, were calculated in Angstrom units (A), and the relative intensities of the lines, I/Io, where Io is one-hundredth of the intensity of the strongest line, above background, were derived with the use of a profile fitting routine. The intensities were uncorrected for Lorentz and polarization effects. The relative intensities are given in terms of the symbols vs = very strong (75-100), s = strong (50-74), m = medium (25-49) and w = weak (0-24). It should be understood that diffraction data listed as single lines may consist of multiple overlapping lines which under certain conditions, such as very high experimental resolution or crystallographic changes, may appear as resolved or partially resolved lines. Typically, crystallographic changes can include minor changes in unit cell parameters and/or a change in crystal symmetry, without a substantial change in structure. These minor effects, including changes in relative intensities, can also occur as a result of differences in cation content, framework composition, nature and degree of pore filling, thermal and/or hydrothermal history, and peak width/shape variations due to particle size/shape effects, structural disorder or other factors known to those skilled in the art of X-ray diffraction.

The material employed in the process of the invention is further characterised by an equilibrium benzene adsorption capacity of greater than about 15 grams benzene/100 grams crystal at 6.7 kPa (50 torr) and 25°C. The equilibrium benzene adsorption capacity characteristic of this material is measured on the basis of no pore blockage by incidental contaminants. For instance, the sorption test will be conducted on the crystalline material phase having any pore blockage contaminants and water removed by ordinary methods. Water may be removed by dehydration techniques, e.g. thermal treatment. Pore blocking inorganic amorphous materials. e.g. silica, and organics may be removed by contact with acid or base or other chemical agents such that the detrital material will be removed without detrimental effect on the crystal of the invention.

The equilibrium benzene adsorption capacity is determined by contacting the material of the invention, after dehydration or calcination at, for example, 450 to 700°C, typically 540°C, for at least one hour and other treatment, if necessary, in an attempt to remove any pore blocking contaminants, at 25°C and 50 torr benzene until equilibrium is reached. The weight of benzene sorbed is then determined as more particularly described hereinafter.

The materials used in the process of the invention are generally mesoporous, by which is meant they have uniform pores within the size range of 13 to 200 Angstroms, more usually 15 to 100 Angstroms. In a preferred embodiment, the material appears to have a hexagonal arrangement of large channels with open internal diameters from 13 to 200 Angstroms. This structure can be revealed by transmission electron microscopy and electron diffraction. Thus, electron micrographs of properly oriented specimens of the material show a hexagonal arrangement of large channels and the corresponding electron diffraction patterns give an approximately hexagonal arrangement of diffraction maxima. The d100 spacing of the electron diffraction patterns is the distance between adjacent spots on the hkO projection of the hexagonal lattice and is related to the repeat distance a0 between channels observed in the electron micrographs through the formula d100 = a0 3/2. This d_{100} spacing observed in the electron diffraction pattern corresponds to the d-spacing of the low angle peak (>18 Angstrom d-spacing) in the X-ray diffraction pattern. The most highly ordered preparations of the material obtained so far have 20-40 distinct spots observable in the electron diffraction patterns. These patterns can be indexed with the hexagonal hkO subset of unique reflections of 100, 110, 200, 210, etc., and their symmetry-related reflections.

The inorganic, non-layered mesoporous crystalline material used in this invention typically has the following composition:

Mn/q(Wa Xb Yc Zd Oh)

wherein W is a divalent element, such as a divalent first row transition metal, e.g. manganese, cobalt and iron, and/or magnesium, preferably cobalt; 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; Z is a pentavalent element, such as phosphorus; M is one or more ions, such as, for example, ammonium, Group IA, IIA and VIIB ions, usually hydrogen, sodium and/or fluoride ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; a, b, c and d are mole fractions of W, X, Y and Z, respectively; h is a number of from 1 to 2.5; and $(a+b+c+d) = 1$.

A preferred embodiment of the above crystalline material is when $(a+b+c)$ is greater than d, and $h = 2$. A further embodiment is when a and $d = 0$, and $h = 2$.

In the as-synthesized form, the material employed in this invention typically has a composition, on an anhydrous basis, expressed empirically as follows:

$$rRMn/q(Wa\ Xb\ Yc\ Zd\ Oh)$$

wherein R is the total organic material not included in M as an ion, and r is the coefficient for R, i.e. the number of moles or mole fraction of R. The M and R components are associated with the material as a result of their presence during crystallization, and are easily removed or, in the case of M, replaced by conventional post-crystallization methods.

Preferably, the crystalline material is a metallosilicate which is synthesized with Bronsted acid active sites by incorporating a tetrahedrally coordinated trivalent element, such as Al, Ga, B, or Fe, within the silicate framework. Aluminosilicate materials of this type are thermally and chemically stable, properties favored for acid catalysis; however, the advantages of mesoporous structures may be utilized by employing highly siliceous materials or crystalline metallosilicate having one or more tetrahedral species having varying degrees of acidity. In addition to the preferred aluminosilicates, the gallosilicate, ferrosilicate and borosilicate materials may be employed. Although matrices may be formed with the germanium analog of silicon, these are expensive and generally no better than the metallosilicates.

Synthesis of the crystalline material employed in the process of the invention is described in detail in our International Patent Publication No. WO 91/11390. In particular, materials having the composition defined by the above formula can be prepared from a reaction mixture having a composition in terms of mole ratios of oxides, within the following ranges:

Reactants	Useful	Preferred
X_2O_3/YO_2	0 to 0.5	0.001 to 0.5
$X_2O_3/(YO_2+Z_2O_5)$	0.1 to 100	0.1 to 20
$X_2O_3/(YO_2+WO+Z_2O_5)$	0.1 to 100	0.1 to 20
Solvent/ $(YO_2+WO+Z_2O_5+X_2O_3)$	1 to 1500	5 to 1000
OH^-/YO_2	0 to 10	0 to 5
$(M_{2/e}O+R_{2/f}O)/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0.01 to 20	0.05 to 5
$M_{2/e}O/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0 to 10	0 to 5
$R_{2/f}O/$ $(YO_2+WO+Z_2O_5+X_2O_3)$	0.01 to 2.0	0.03 to 1.0

wherein e and f are the weighted average valences of M and R, respectively, wherein the solvent is a C_1 to C_6 alcohol or diol, or, more preferably, water and wherein R comprises an organic directing agent having the formula $R_1R_2R_3R_4Q^+$ wherein Q is nitrogen or phosphorus and wherein at least one of R_1, R_2, R_3 and R_4 is aryl or alkyl group having 6 to 36 carbon atoms, e.g. $-C_6H_{13}$, $-C_{10}H_{21}$, $-C_{16}H_{33}$ and $-C_{18}H_{37}$, and each of the remainder of R_1, R_2, R_3 and R_4 is selected from hydrogen and an alkyl group having 1 to 5 carbon atoms. The compound from which the above ammonium or phosphonium ion is derived may be, for example, the hydroxide, halide, silicate or mixtures thereof.

The particular effectiveness of the above directing agent, when compared with other such agents known to direct synthesis of one or more other crystal structures, is believed due to its ability to function as a template in the nucleation and growth of the desired ultra-large pore materials. Non-limiting examples of these directing agents include cetyltrimethylammonium, cetyltrimethylphosphonium, octadecyltrimethylphosphonium, benzyltrimethylammonium, cetylpyridinium, myristyltrimethylammonium, decyltrimethylammonium, dodecyltrimethylammonium and dimethyldidodecylammonium compounds.

Preferably, the total organic, R, present in the reaction mixture comprises an additional organic directing agent in the form of an ammonium or phosphonium ion of the above directing agent formula but wherein each R_1, R_2, R_3 and R_4 is selected from hydrogen and an alkyl group of 1 to 5 carbon atoms (2 of the alkyl groups can be interconnected to form a cyclic compound). Examples of the additional organic directing agent include tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium and pyrrolidinium compounds. The molar ratio of the first-mentioned organic directing agent to the additional organic directing agent can be in the range 100/1 to 0.01/1. Where the additional organic directing agent is present, the molar ratio $R_{2/f}O/(YO_2+WO+Z_2O_5+X_2O_3)$ in the reaction mixture is preferably 0.1 to 2.0, most preferably 0.12 to 1.0.

In addition, to vary the pore size of the final crystalline phase material, the total organic, R, in the reaction mixture can include an auxiliary organic in addition to the organic directing agent(s) described above. This auxiliary organic is selected from (1) aromatic hydrocarbons and amines having 5-20 carbon atoms and halogen- and C_1-C_{14} alkyl-substituted derivatives thereof, (2) cyclic and polycyclic aliphatic hydrocarbons and amines of 5 to 20 carbon atoms and halogen- and C_1-C_{14} alkyl-substituted derivatives thereof and (3) straight and branched chain aliphatic hydrocarbons and amines having 3-16 carbon atoms and halogen-substituted derivatives thereof.

In the above auxiliary organics, the halogen substituent is preferably bromine. The C_1-C_{14} alkyl substituent may be a linear or branched aliphatic chain, such as, for example, methyl, ethyl, propyl, isopropyl, butyl, pentyl and combinations thereof. Examples of these auxiliary organics include, for example, p-xylene, trimethylbenzene, triethylbenzene and triisopropylbenzene.

With the inclusion of the auxiliary organic in the reaction mixture, the mole ratio of auxiliary organic/YO_2 will be from 0.05 to 20, preferably from 0.1 to 10, and the mole ratio of auxiliary organic/organic directing agent(s) will be from 0.02 to 100, preferably from 0.05 to 35.

When a source of silicon is used in the synthesis method, it is preferred to use at least in part an organic silicate, such as, for example, a quaternary ammonium silicate. Non-limiting examples of such a silicate include tetramethylammonium silicate and tetraethylorthosilicate.

Non-limiting examples of various combinations of W, X, Y and Z contemplated for the above reaction mixture include:

W	X	Y	Z
--	Al	Si	--
--	Al	--	P
--	Al	Si	P
Co	Al	--	P
Co	Al	Si	P
--	--	Si	--

including the combinations of W being Mg, or an element selected from the divalent first row transition metals, e.g. Mn, Co and Fe; X being B, Ga or Fe; and Y being Ge.

To produce the crystalline material of the invention, the reaction mixture described above is maintained at a temperature of 25 to 250°C, preferably 50 to 175°C, and preferably a pH of 9 to 14 for a period of time until the required crystals form, typically 5 minutes to 14 days, more preferably 1 to 300 hours.

When the crystalline material of the invention is an aluminosilicate, the synthesis method conveniently involves the following steps:

(1) Mix the organic (R) directing agent with the solvent or solvent mixture such that the mole ratio of solvent/$R_{2/f}O$ is within the range of 50 to 800, preferably from 50 to 500. This mixture constitutes the "primary template" for the synthesis method.

(2) To the primary template mixture of step (1) add the silica and alumina such that the ratio of $R_{2/f}O/(SiO_2+Al_2O_3)$ is within the range 0.01 to 2.0.

(3) Agitate the mixture resulting from step (2) at a temperature of 20 to 40°C, preferably for 5 minutes to 3 hours.

(4) Allow the mixture to stand with or without agitation, preferably at 20 to 50°C, and preferably for 10 minutes to 24 hours.

(5) Crystallize the product from step (4) at a temperature of 50 to 150°C, preferably for 1 to 72 hours.

Normally, the crystals of the mesoporous support material will be composited with a matrix material to form the finished catalyst and for this purpose conventional matrix materials such as alumina, silica-alumina and silica are suitable with preference given to silica as a non-acidic binder. Other binder materials may be used, for example, titania, zirconia and othe metal oxides or clays. The mesoporous material is usually composited with the matrix in amounts from 80:20 to 20:80 by weight, typically from 80:20 to 50:50 mesoporous material:matrix. Compositing may be done by conventional means including mulling the materials together followed by extrusion of pelletizing into the desired finished catalyst particles. A preferred method for extrusion with silica as a binder is disclosed in U.S. 4,582,815. If the catalyst is to be steamed in order to achieve the desired low acidity, it is performed after the catalyst has been formulated with the binder, as is conventional.

The catalyst may be treated by conventional presulfiding treatments, e.g. by heating in the presence of hydrogen sulfide, to convert oxide forms of the metal components to their corresponding sulfides.

The invention will now be more particularly described with reference to the Examples and the accompanying drawings, in which Figures 1 and 2 are graphs showing the relative isomerization performance of the present catalysts and comparative catalysts.

Examples 1 to 19 below illustrate the preparation of the mesoporous crystalline materials used to prepare the catalysts. In these examples, the sorption data for water, cyclohexane, benzene and/or n-hexane, they are Equilibrium Adsorption values determined as follows:

A weighed sample of the adsorbent, after calcination at about 540°C for at least about 1 hour and other treatment, if necessary, to remove any pore blocking contaminants, is contacted with the desired pure adsorbate vapor in an adsorption chamber. The increase in weight of the adsorbent is calculated as the adsorption capacity of the sample in terms of grams/100 grams adsorbent based on adsorbent weight after calcination at about 540°C. The present composition exhibits an equilibrium benzene adsorption capacity at (6.7 kPa) 50 Torr and 25°C of greater than about 15 grams/100 grams, particularly greater than about 17.5 grams/100 grams and more particularly greater than about 20 grams/100 grams.

A preferred way to determine equilibrium adsorption values is to contact the desired pure adsorbate vapor in an adsorption chamber evacuated to less than 1 mm at conditions of 1.6 kPa (12 Torr) of water vapor, 5.3 kPa (40 Torr) of n-hexane or cyclohexane vapor, or 6.7 kPa (50 Torr) of benzene vapor, at 25°C. The pressure is kept constant (within about + 0.5 mm) by addition of adsorbate vapor controlled by a manostat during the adsorption period. As adsorbate is adsorbed by the crystalline material, the decrease in pressure causes the manostat to open a valve which admits more adsorbate vapor to the chamber to restore the above control pressures. Sorption is complete when the pressure change is not sufficient to activate the manostat.

Another method for benzene adsorption data is on a suitable thermogravimetric analysis system, such as a computer-controlled 990/951 duPont TGA system. The adsorbent sample is dehydrated (physically sorbed water removed) by heating at, for example, about 350°C or 500°C to constant weight in flowing helium. If the sample is in as-synthesized form, e.g. containing organic directing agents, it is calcined at about 540°C in air and held to constant weight instead of the previously described 350°C or 500°C treatment. Benzene adsorption isotherms are measured at 25°C by blending a benzene saturated helium gas stream with a pure helium gas stream in the proper proportions to obtain the desired benzene partial pressure. The value of the adsorption at 6.7 kPa (50 Torr) of benzene is taken from a plot of adsorption isotherm.

In the examples, percentages are by weight unless otherwise indicated.

EXAMPLE 1

One hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution, prepared by contacting a 29 wt.% N,N,N- trimethyl-1-hexadecanaminium chloride solution with a hydroxide-for-halide exchange resin, was combined with 100 grams of an aqueous solution of tetramethylammonium (TMA) silicate (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing about 6 wt.% free water and about 4.5 wt.% bound water of hydration and having an ultimate particle size of about 0.02 micron, was added. The resulting mixture was placed in a polypropylene bottle, which was placed in a steam box at 95°C overnight. The mixture had a composition in terms of moles per mole Al_2O_3:

2.7	moles Na_2O
392	moles SiO_2
35.7	moles $(CTMA)_2O$
61.7	moles $(TMA)_2O$
6231	moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 475 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	8.3
Cyclohexane	22.9
n-Hexane	18.2
Benzene	21.5

The product of this example may be characterized by X-ray diffractiion as including a very strong relative intensity line at 37.8 ± 2.0 Å d-spacing, and weak lines at 21.6 ± 1.0 and 19.2 ± 1.0 Å. Transmission electron microscopy (TEM) produced images of a hexagonal arrangement of uniform pores and hexagonal electron diffraction pattern with a d_{100} value of about 39 Å.

EXAMPLE 2

One hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 100 grams of an aqueous solution of tetramethylammonium (TMA) hydroxide (25%) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing about 6 wt.% free water and about 4.5 wt.% bound water of hydration and having an ultimate particle size of about 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C overnight. The mixture had a composition in terms of moles per mole Al_2O_3:

2.7	moles Na_2O
291	moles SiO_2
35.7	moles $(CTMA)_2O$
102	moles $(TMA)_2O$
6120	moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 993 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	7.1
Cyclohexane	47.2
n-Hexane	36.2
Benzene	49.5

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 39.3 ± 2.0 Å d-spacing, and weak lines at 22.2 ± 1.0 and 19.4 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

A portion of the above product was then contacted with 100% steam at 790°C (1450°F) for two hours. The surface area of the steamed material was measured to be 440 m^2/g, indicating that about 45% was retained following severe steaming.

Another portion of the calcined product of this example was contacted with 100% steam at 680°C (1250°F) for two hours. The surface area of this material was measured to be 718 m^2/g, indicating that 72% was retained after steaming at these conditions.

EXAMPLE 3

Water, cetyltrimethylammonium hydroxide solution prepared as in Example 1, aluminum sulfate, HiSil and an aqueous solution of tetrapropylammonium (TPA) bromide (35%) were combined to produce a mixture having a composition in terms of moles per mole Al_2O_3:

0.65	moles Na_2O
65	moles SiO_2
8.8	moles $(CTMA)_2O$
1.22	moles $(TPA)_2O$
1336	moles H_2O

The resulting mixture was placed in a polypropylene bottle, which was kept in a steam box at 95°C for 192 hours. The sample was then cooled to room temperature and combined with CTMA hydroxide solution prepared as in Example 1 and TMA hydroxide (25% by weight) in the weight ratio of 3 parts mixture, 1 part CTMA hydroxide and 2 parts TMA hydroxide. The combined mixture was then placed in a polypropylene bottle and kept in a steam box at 95°C overnight. The combined mixture had a composition in terms of moles per mole Al_2O_3:

0.65	moles	Na_2O
65	moles	SiO_2
15	moles	$(CTMA)_2O$
1.22	moles	$(TPA)_2O$
35.6	moles	$(TMA)_2O$
2927	moles	H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 1085 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	11.5
Cyclohexane	> 50
n-Hexane	39.8
Benzene	62

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 38.2 ± 2.0 Å d-spacing, and weak lines at 22.2 ± 1.0 and 19.4 ± 1.0 Å. TEM indicated the product contained the ultra-large pore material.

EXAMPLE 4

Two hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 2 grams of Catapal alumina (alpha-alumina monohydrate, 74% alumina) and 100 grams of an aqueous solution of tetramethylammonium (TMA) silicate (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing about 6 wt.% free water and about 4.5 wt.% bound water of hydration and having an ultimate particle size of about 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C for 48 hours. The mixture had a composition in terms of moles per mole Al_2O_3:

0.23 moles Na_2O
33.2 moles SiO_2
6.1 moles $(CTMA)_2O$
5.2 moles $(TMA)_2O$
780 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 1043 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	6.3
Cyclohexane	> 50
n-Hexane	49.1
Benzene	66.7

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 40.8 ± 2.0 Å d-spacing, and weak lines at 23.1 ± 1.0 and 20.1 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

EXAMPLE 5

Two-hundred sixty grams of water was combined with 77 grams of phosphoric acid (85%), 46 grams of Catapal alumina (74% alumina), and 24 grams of pyrrolidine (Pyr) with stirring. This first mixture was placed in a stirred autoclave and heated to 150°C for six days. The material was filtered, washed and air-dried. Fifty grams of this product was slurried with 200 grams of water and 200 grams of cetyltrimethylammonium hydroxide solution prepared as in Example 1. Four hundred grams of an aqueous solution of tetraethylammonium silicate (10% silica) was then added to form a second mixture which was placed in a polypropylene bottle and kept in a steam box at 95°C overnight. The first mixture had a composition in terms of moles per mole Al_2O_3:

1.0 moles P_2O_5
0.51 moles $(Pyr)_2O$
47.2 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 707 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	33.2
Cyclohexane	19.7
n-Hexane	20.1
Benzene	23.3

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 25.4 ± 1.5 Å d-spacing. TEM indicated the product contained the present ultra-large pore material.

EXAMPLE 6

A solution of 1.35 grams of $NaAlO_2$ (43.5% Al_2O_3, 30% Na_2O) dissolved in 45.2 grams of water was mixed with 17.3 grams of NaOH, 125.3 grams of colloidal silica (40%, Ludox HS-40) and 42.6 grams of 40% aqueous solution of tetraethylammonium (TEA) hydroxide. After stirring overnight, the mixture was heated for 7 days in a steam box (95°C). Following filtration, 151 grams of this solution was mixed with 31 grams of cetyltrimethylammonium hydroxide solution prepared as in Example 1 and stored in the steam box at 95°C for 13 days. The mixture had the following relative molar composition:

0.25 moles Al_2O_3
10 moles Na_2O
36 moles SiO_2
0.95 moles $(CTMA)_2O$
2.5 moles $(TEA)_2O$
445 moles H_2O

The resulting solid product was recovered by filtration and washed with water and ethanol. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product composition included 0.14 wt.% Na, 68.5 wt.% SiO_2 and 5.1 wt.% Al_2O_3, and proved to have a benzene equilibrium adsorption capacity of 58.6 grams/100 grams.

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 31.4 ± 1.5 Å d-spacing. TEM indicated that the product contained the present ultra-large pore material.

EXAMPLE 7

A mixture of 300 grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 and 41 grams of colloidal silica (40%, Ludox HS-40) was heated in a 600 cc autoclave at 150°C for 48 hours with stirring at 200 rpm. The mixture has a composition in terms of moles per mole SiO_2:

0.5 mole $(CTMA)_2O$
46.5 moles H_2O

The resulting solid product was recovered by filtration, washed with water, then calcined at 540°C for 1 hour in nitrogen, followed by 10 hours in air.

The calcined product composition included less than 0.01 wt.% Na, about 98.7 wt.% SiO_2 and about 0.01 wt.% Al_2O_3, and proved to have a surface area of 896 m^2/g. The calcined product had the following equilibrium adsorption capacities in grams/100 grams:

H_2O	8.4
Cyclohexane	49.8
n-Hexane	42.3
Benzene	55.7

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 40.0 ± 2.0 Å d-spacing and a weak line at 21.2 ± 1.0 Å. TEM indicated that the product of this example contained at least three separate phases, one of which was the ultra-large pore material.

EXAMPLE 8

A mixture of 150 grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 and 21 grams of colloidal silica (40%, Ludox HS-40) with an initial pH of 12.64 was heated in a 300 cc autoclave at 150°C for 48 hours with stirring at 200 rpm. The mixture had a composition in terms of moles per mole SiO_2:

0.5 mole $(CTMA)_2O$
46.5 moles H_2O

The resulting solid product was recovered by filtration, washed with water, then calcined at 540°C for 6 hours in air.

The calcined product composition was measured to include 0.01 wt.% Na, 93.2 wt.% SiO_2 and 0.016 wt.% Al_2O_3, and proved to have a surface area of 992 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	4.6
Cyclohexane	> 50
n-Hexane	> 50
Benzene	62.7

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 43.6 ± 2.0 Å d-spacing and weak lines at 25.1 ± 1.5 and 21.7 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

EXAMPLE 9

Sodium aluminate (4.15g) was added slowly into a solution containing 16g of myristyltrimethylammonium bromide (C_{14}TMABr) in 100g of water. Tetramethylammonium silicate (100g-10% SiO_2), HiSil (25g) and tetramethylammonium hydroxide (14.2g-25% solution) were then added to the mixture. The mixture was crystallized in an autoclave at 120°C with stirring for 24 hours.

The product was filtered, washed and air dried. Elemental analysis showed the product contained 53.3 wt% SiO_2, 3.2 wt% Al_2O_3, 15.0 wt% C, 1.88 wt% N, 0.11 wt% Na and 53.5 wt% ash at 1000°C. The X-ray diffraction pattern of the material after calcination at 540°C for 1 hour in N_2 and 6 hours in air includes a very strong relative intensity line at 35.3 ± 2.0 Å d-spacing and weak lines at 20.4 ± 1.0 and 17.7 ± 1.0 Å d-spacing. TEM indicated that the product contained the ultra-large pore material.

The washed product, having been exchanged with 1N ammonium nitrate solution at room temperature, then calcined, proved to have a surface area of 827 m^2/g and the following equilibrium adsorption capacities in g/100g anhydrous sorbent:

H_2O	30.8
Cyclohexane	33.0
n-Hexane	27.9
Benzene	40.7

EXAMPLE 10

Sodium aluminum (4.15g) was added slowly into a solution containing 480g of dodecyltrimethylammonium hydroxide (C_{12}TMAOH, 50%) solution diluted with 120g of water. UltraSil (50g) and an aqueous solution of tetramethylammonium silicate (200g-10% SiO_2) and tetramethylammonium hydroxide (26.38g-25% solution) were then added to the mixture. The mixture was crystallized in an autoclave at 100°C with stirring for 24 hours.

The product was filtered, washed and air dried. After calcination at 540°C for 1 hour in N_2 and 6 hours in air, the X-ray diffraction pattern includes a very strong relative intensity line at 30.4 ± 1.5 Å d-spacing and weak lines at 17.7 ± 1.0 and 15.3 ± 1.0 Å d-spacing. TEM indicated that the product contained the ultra-large pore material.

The washed product, having been exchanged with 1N ammonium nitrate solution at room temperature, then calcined, proved to have a surface area of 1078 m^2/g and the following equilibrium adsorption capacities in g/100g anhydrous sorbent:

H_2O	32.6
Cyclohexane	38.1
n-Hexane	33.3
Benzene	42.9

EXAMPLE 11

A solution of 4.9 grams of $NaAlO_2$ (43.5 % Al_2O_3, 30% NaO_2) in 37.5 grams of water was mixed with 46.3 cc of 40% aqueous tetraethylammonium hydroxide solution and 96 grams of colloidal silica (40%, Ludox HS-40). The gel was stirred vigorously for 0.5 hour, mixed with an equal volume (150 ml) of cetyltrimethylammonium hydroxide solution prepared as in Example 1 and reacted at 100°C for 168 hours. The mixture had the following composition in terms of moles per mole Al_2O_3:

1.1	moles Na_2O
30.6	moles SiO_2
3.0	moles $(TEA)_2O$
3.25	moles $(CTMA)_2O$
609	moles H_2O

The resulting solid product was recovered by filtration, washed with water then calcined at 540°C for 16 hours in air. The calcined product proved to have a surface area of 1352 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	23.6
Cyclohexane	>50
n-Hexane	49
Benzene	67.5

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 38.5 ± 2.0 Å d-spacing and a weak line at 20.3 ± 1.0 Å. TEM indicated that the product contained the ultra-large pore material.

EXAMPLE 12

Two hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 4.15 grams of sodium aluminate and 100 grams of aqueous tetramethylammonium (TMA) silicate solution (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing about 6 wt.% free water and about 4.5 wt.% bound water of hydration and having an ultimate particle size of about 0.02 micron, was added. The resulting mixture was placed in a static autoclave at 150°C for 24 hours. The mixture had a composition in terms of moles per mole Al_2O_3:

1.25 moles Na_2O
27.8 moles SiO_2
5.1 moles $(CTMA)_2O$
4.40 moles $(TMA)_2O$
650 moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. TEM indicated that this product contained the ultra-large pore material. The X-ray diffraction pattern of the calcined product of this example can be characterized as including a very strong relative intensity line at

44.2 ± 2.0 Å d-spacing and weak lines at 25.2 ± 1.5 and 22.0 ± 1.0 Å.

The calcined product proved to have a surface area of 932 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	39.3
Cyclohexane	46.6
n-Hexane	37.5
Benzene	50

EXAMPLE 13

Two hundred grams of cetyltrimethylammonium (CTMA) hydroxide solution prepared as in Example 1 was combined with 4.15 grams of sodium aluminate and 100 grams of aqueous tetramethylammonium (TMA) silicate solution (10% silica) with stirring. Twenty-five grams of HiSil, a precipitated hydrated silica containing about 6 wt.% free water and about 4.5 wt.% bound water of hydration and having an ultimate particle size of about 0.02 micron, was added. The resulting mixture was placed in a steam box at 100°C for 48 hours. The mixture had a composition in terms of moles per mole Al_2O_3:

1.25	moles Na_2O
27.8	moles SiO_2
5.1	moles $(CTMA)_2O$
4.4	moles $(TMA)_2O$
650	moles H_2O

The resulting solid product was recovered by filtration and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air. The calcined product proved to have the following equilibrium adsorption capacities in grams/100 grams:

H_2O	35.2
Cyclohexane	> 50
n-Hexane	40.8
Benzene	53.5

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 39.1 ± 2.0 Å d-spacing and weak lines at 22.4 ± 1.0 and 19.4 ± 1.0 Å. TEM indicated that this product contained the ultra-large pore material.

EXAMPLE 14

A mixture of 125 grams of 29% CTMA chloride aqueous solution, 200 grams of water, 3 grams of sodium aluminate (in 50 grams H_2O), 65 grams of Ultrasil, amorphous precipitated silica available from PQ Corporation, and 21 grams NaOH (in 50 grams H_2O) was stirred thoroughly and crystallized at 150°C for 168 hours. The reaction mixture had the following relative molar composition in terms of moles per mole silica:

0.10	moles $(CTMA)_2O$
21.89	moles H_2O
0.036	moles $NaAlO_2$
0.53	moles NaOH

The solid product was isolated by filtration, washed with water, dried for 16 hours at room temperature and calcined at 540°C for 10 hours in air. The calcined product proved to have a surface area of 840 m^2/g, and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	15.2
Cyclohexane	42.0
n-Hexane	26.5
Benzene	62

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 40.5 ± 2.0 Å d-spacing. TEM indicated that the product contained the ultra-large pore material.

EXAMPLE 15

To make the primary template mixture for this example, 240 grams of water was added to a 92 gram solution of 50% dodecyltrimethylammonium hydroxide, 36% isopropyl alcohol and 14% water such that the mole ratio of Solvent/$R_{2/f}O$ was 155. The mole ratio of $H_2O/R_{2/f}O$ in this mixture was 149 and the IPA/$R_{2/f}O$ mole ratio was 6. To the primary template mixture was added 4.15 grams of sodium aluminate, 25 grams of HiSil, 100 grams of aqueous tetramethylammonium silicate solution (10% SiO_2) and 13.2 grams of 25% aqueous tetramethylammonium hydroxide solution. The mole ratio of $R_{2/f}O/(SiO_2+Al_2O_3)$ was 0.28 for the mixture.

This mixture was stirred at 25°C for 1 hour. The resulting mixture was then placed in an autoclave at 100°C and stirred at 100 rpm for 24 hours. The mixture in the autoclave had the following relative molar composition in terms of moles per mole SiO_2:

0.05	mole Na_2O
0.036	mole Al_2O_3
0.18	mole $(C_{12}TMA)_2O$
0.12	mole $(TMA)_2O$
36.0	moles H_2O
1.0	mole IPA

The resulting solid product was recovered by filtration, washed with water and dried in air at ambient temperature. The product was then calcined at 540°C for 1 hour in nitrogen, followed by 6 hours in air.

The calcined product proved to have a surface area of 1223 m^2/g and the following equilibrium adsorption capacities in grams/100 grams:

H_2O	25.5
Cyclohexane	41.1
n-Hexane	35.1
Benzene	51

The X-ray diffraction pattern of the calcined product may be characterized as including a very strong relative intensity line at 30.8 ± 1.5 Å d-spacing and weak lines at 17.9 ± 1.0 and 15.5 ± 1.0 Å. TEM indicated this product to contain the ultra-large pore material.

EXAMPLE 16

A 50.75 gram quantity of decyltrimethylammonium hydroxide (prepared by contacting a ca. 29 wt.% solution of decyltrimethylammonium bromide with a hydroxide-for-halide exchange resin) was combined with 8.75 grams of tetraethylorthosilicate. The mixture was stirred for about 1 hour and then transferred to a polypropylene jar which was then placed in a steambox for about 24 hours. The mixture had a composition in terms of moles per mole SiO_2:

0.81 mole $(C_{10}TMA)_2O$
47.6 moles H_2O

The resulting solid product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2/air mixture and then held in air for about 8 hours. The calcined product proved to have a surface area of 915 m^2/g and an equilibrium benzene adsorption capacity of 35 grams/100 grams. Argon physisorption data indicated an argon uptake of 0.34 cc/gram, and a pore size of 15 Å.

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 27.5 ± 1.5 Å d-spacing and weak lines at 15.8 ± 1.0 and 13.7 ± 1.0 Å. TEM indicated that the product of this example contained the ultra-large pore material.

EXAMPLE 17

To eighty grams of cetyltrimethylammonium hydroxide (CTMAOH) solution prepared as in Example 1 was added 1.65 grams of $NaAlO_2$. The mixture was stirred at room temperature until the $NaAlO_2$ was dissolved. To this solution was added 40 grams of aqueous tetramethylammonium (TMA) silicate solution (10 wt.% SiO_2), 10 grams of HiSil, 200 grams of water and 70 grams of 1,3,5-trimethylbenzene (mesitylene). The resulting mixture was stirred at room temperature for several minutes. The gel was then loaded into a 600 cc autoclave and heated at 105°C for sixty-eight hours with stirring at 150 rpm. The mixture had a composition in terms of moles per mole Al_2O_3:

1.25	moles	Na_2O
27.8	moles	SiO_2
5.1	moles	$(CTMA)_2O$
2.24	moles	$(TMA)_2O$
2256	moles	H_2O
80.53	moles	1,3,5-trimethylbenzene

The resulting product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2/air mixture and then held in air for about 10 hours. The calcined product proved to have an equilibrium benzene adsorption capacity of >25 grams/100 grams.

The X-ray diffraction pattern of the calcined product may be characterized as including a broad, very strong relative intensity line at about 102 Å d-spacing, but accurate positions of lines in the extreme low angle region of the X-ray diffraction pattern are very difficult to determine with conventional X-ray diffractometers. Furthermore, finer collimating slits were required to resolve a peak at this low 2-theta angle. The slits used in this example, starting at the X-ray tube, were 0.1, 0.3, 0.5

and 0.2 mm, respectively. TEM indicated that the product of this example contained several materials with different d_{100} values as observed in their electron diffraction patterns. These materials were found to possess d_{100} values between about 85 Å d-spacing and about 120 Å d-spacing.

EXAMPLE 18

To eighty grams of cetyltrimethylammonium hydroxide (CTMAOH) solution prepared as in Example 1 was added 1.65 grams of $NaAlO_2$. The mixture was stirred at room temperature until the $NaAlO_2$ was dissolved. To this solution was added 40 grams of aqueous tetramethylammonium (TMA) silicate solution (10 wt.% SiO_2), 10 grams of HiSil, 200 grams of water and 120 grams of 1,3,5-trimethylbenzene (mesitylene). The resulting mixture was stirred at room temperature for several minutes. The gel was then loaded into a 600 cc autoclave and heated at 105°C for ninety hours with stirring at 150 rpm. The mixture had a composition in terms of moles per mole Al_2O_3:

1.25	moles Na_2O
27.8	moles SiO_2
5.1	moles $(CTMA)_2O$
2.24	moles $(TMA)_2O$
2256	moles H_2O
132.7	moles 1,3,5-trimethylbenzene

The resulting product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2/air mixture and then held in air for about 10 hours. The calcined product proved to have a surface area of 915 m^2/g and an equilbrium benzene adsorption capacity of >25 grams/100 grams. Argon physisorption data indicated an argon uptake of 0.95 cc/gram, and a pore size centered on 78 Å (Dollimore-Heal Method, see Example 22(b)), but running from 70 to greater than 105 Angstoms. The X-ray diffraction pattern of the calcined product of this example may be characterized as having only enhanced scattered intensity in the very low angle region of the X-ray diffraction, where intensity from the transmitted incident X-ray beam is usually observed. However, TEM indicated that the product contained several materials with different d_{100} values as observed in their electron diffraction patterns. These materials were found to possess d_{100} values between about 85 Å d-spacing and about 110 Å d-spacing.

EXAMPLE 19

To eighty grams of cetyltrimethylammonium hydroxide (CTMAOH) solution prepared as in Example 1 was added 1.65 grams of $NaAlO_2$. The mixture was stirred at room temperature until the $NaAlO_2$ was dissolved. To this solution was added 40 grams of aqueous tetramethylammonium (TMA) silicate solution (10 wt.% SiO_2), 10 grams of HiSil, and 18 grams of 1,3,5-trimethylbenzene (mesitylene). The resulting mixture was stirred at room temperature for several minutes. The gel was then loaded into a 300 cc autoclave and heated at 105°C for four hours with stirring at 150 rpm. The mixture had a composition in terms of moles per mole Al_2O_3:

1.25	moles Na_2O
27.8	moles SiO_2
5.1	moles $(CTMA)_2O$
2.24	moles $(TMA)_2O$
650	moles H_2O
19.9	moles 1,3,5-trimethylbenzene

The resulting product was filtered and washed several times with warm (60-70°C) distilled water and with acetone. The final product was calcined to 538°C in N_2/air mixture and then held in air for about 8 hours.

The calcined product proved to have a surface area of 975 m^2/g and an equilibrium benzene adsorption capacity of >40 grams/100 grams. Argon physisorption data indicated an argon uptake of 0.97 cc/gram, and a pore size of 63 Å (Dollimore-Heal Method), with the peak occurring at $P/P_O=0.65$.

The X-ray diffraction pattern of the calcined product of this example may be characterized as including a very strong relative intensity line at 63 ± 5 Å d-spacing and weak lines at 36.4 ± 2.0, 31.3 ± 1.5 Å and 23.8 ± 1.0 Å d-spacing. TEM indicated that the product of this example contained the ultra-large pore material.

EXAMPLE 20

Argon Physisorption Determination

To determine the pore diameters of the mesoporous products with pores up to about 60 Å in diameter, 0.2 gram samples of the products of Examples 1 through 17 were placed in glass sample tubes and attached to a physisorption apparatus as described in U.S. Patent No. 4,762,010.

The samples were heated to 300°C for 3 hours in vacuo to remove adsorbed water. Thereafter, the samples were cooled to 87°K by immersion of the sample tubes in liquid argon. Metered amounts of gaseous argon were then admitted to the samples in stepwise manner as described in U.S. Patent No. 4,762,010, column 20. From the amount of argon admitted to the samples and the amount of argon left in the gas space above the samples, the amount of argon adsorbed can be calculated. For this calculation, the ideal gas law and the calibrated sample volumes were used. (See also S.J. Gregg et al., Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, 1982). In each instance, a graph of the amount adsorbed versus the relative pressure above the sample, at equilibrium, constitutes the adsorption isotherm. It is common to use relative pressures which are obtained by forming the ratio of the equilibrium pressure and the vapor pressure P_o of the adsorbate at the temperature where the isotherm is measured. Sufficiently small amounts of argon were admitted in each step to generate 168 data points in the relative pressure range from 0 to 0.6. At least about 100 points are required to define the isotherm with sufficient detail.

The step (inflection) in the isotherm, indicates filling of a pore system. The size of the step indicates the amount adsorbed, whereas the position of the step in terms of P/P_o reflects the size of the pores in which the adsorption takes place. Larger pores are filled at higher P/P_o. In order to better locate the position of the step in the isotherm, the derivative with respect to log (P/P_o) is formed. The adsorption peak (stated in terms of log (P/P_o)) may be related to the physical pore diameter (Å) by the following formula:

$$\log(P/P_o) = \frac{K}{d-0.38}\left[\frac{S^4}{3(L-D/2)^3} - \frac{S^{10}}{9(L-D/2)^9} - \frac{S^4}{3(D/2)^3} + \frac{S^{10}}{9(D/2)^9}\right]$$

where d = pore diameter in nanometers, K = 32.17, S = 0.2446, L = d + 0.19, and D = 0.57.

This formula is derived from the method of Horvath and Kawazoe (G. Horvath et al., J. Chem. Eng. Japan, 16 (6) 470(1983)). The constants required for the implementation of this formula were determined from a measured isotherm of ALPO-5 and its known pore size. This method is particularly useful for microporous materials having pores of up to about 60 Å in diameter.

The results of this procedure for the samples from Examples 1 through 17 are tabulated below. The samples from Examples 10, 13 and 15 gave two separate peaks, believed to be the result of two separate ultra-large pore phases in the products.

Example	Pore Diameter, Å
1	32.2
2	35.4
3	42.5
4	39.6
5	16.9
6	27.3
7	36.6
8	42.6
9	28.3
10	22.8, 30.8
11	36.8
12	36.1
13	35.0, 42.1
14	40.0
15	22.4, 30.4
16	15.0

EXAMPLE 21

The following mixture (parts by weight) was charged to an autoclave:

48 parts Cetyltrimethylammonium (CTMA) hydroxide solution, prepared by contacting a 29wt.% N,N,N-trimethyl-1-hexadecylammonium chloride solution with a hydroxide-for-halide exchange resin 1 part Sodium aluminate, 24 parts Tetramethylammonim silicate (10% aqueous solution), 6 parts Precipitated hydrated silica (HiSil♦).

The mixture was crystallized at 100°C for 20 hrs. with stirring under autogeneous pressure, and the resulting product was recovered by filtration and dried in air at ambient temperature. A sample of the product was calcined at 540° C in nitrogen followed air.

The calcined product had a surface area of 1120 m2/g and the following equilibrium absorption capacities in grams/100 grams:

H2O	10.8
Cyclohexane	>50
n-hexane	>50
Benzene	67

The product exhibited a very strong relative intensity line at 38.4 + 2.0 Å d-spacing, and weak lines at 22.6 + 1.0, 20.0 + 1.0, and 15.2 +1.0 Å.

An unbound Pt/H-MCM-41 catalyst containing 0.6 wt% platinum was prepared by subjecting the calcined product to ammonium exchange in buffered solution at pH=8 to remove sodium, followed by exchange with $Pt(NH_3)_4Cl_2$ in the presence of ammonium ions at pH 4-5, followed by drying and calcination. An amorphous silica-alumina catalyst containing 0.6 wt% platinum, comparable to commercial isomerization catalysts, was also prepared for comparison.

The two catalysts were evaluated for paraffin isomerization using a micro unit equipped with a 12.5 mm downflow stainless steel reactor. In a typical experiment, 10 cc of sized catalyst (14/24 mesh) were loaded into the reactor and reduced in hydrogen at 800°F (427°C) for two hours. The reactor was cooled to 450°F (232°C) and pressurized to 100 psig (790 kpa abs.) with hydrogen. N-hexane as feed was then introduced at 1 WHSV with a 2:1 mol:mol hydrogen cofeed. The product from the reactor was analyzed with an on-line gas chromatograph equipped with a 30 meter megabore DB-1 column.

The yields of isoparaffin product with the two catalysts are plotted as a function of n-hexane conversion in Figure 1 of the drawings. The Pt/MCM-41 catalyst gave a higher yield of isoparaffins than the Pt/silica-alumina catalyst at equivalent n-hexane conversion. Figure 2 shows the light gas yield (C_5^-) as a function of n-hexane conversion for both catalysts. The Pt/MCM-41 catalyst clearly produces less cracked product at equivalent n-hexane conversion, demonstrating that the catalyst based on the ultra large pore material is more selective for isoparaffin when compared to the amorphous catalyst. The distribution of products for the two catalysts at 650°F operating temperature are shown in Table 1 below.

TABLE 1

Isomerate Products at 650°F (343°C)

Catalyst	Pt/MCM-41	Pt/SiO_2-Al_2O_3
Feed Rate (gm n-C_6/gm Cat/hr)	1.0	1.0
Hours On-Stream	129	64
Conversion, wt%	74.6	78.6
Product Distribution, wt%		
C_5-	2.3	8.8
n-Hexane	25.4	21.4
Methylpentanes	53.7	49.9
Dimethylbutanes	18.2	18.5
Methylcyclopentane	0.2	0.5
C_7+	0.2	0.9

CLAIMS:

1. A process for isomerizing paraffins comprising contacting a paraffin feed with an isomerization catalyst comprising a hydrogenation/ dehydrogenation component on a porous support which includes an inorganic, porous, non-layered crystalline phase material exhibiting, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Angstrom Units with a relative intensity of 100 and having a benzene adsorption capacity of greater than 15 grams of benzene per 100 grams of said material at 6.7 kPa (50 torr) and 25°C.

2. A process according to claim 1 in which the feed comprises a C_4-C_8 linear paraffin.

3. A process according to claim 1 which is carried out at a temperature of 90 to 425°C (200 to 800°F).

4. A process according to claim 1 which is carried out at a pressure of 100 to 7000 kPa (atmospheric to 1000 psig).

5. A process according to claim 1 which is carried out in the presence of hydrogen.

6. A process according to claim 5 which is carried out in the presence of hydrogen at a molar ratio of from 0.1:1 to 10:1 (hydrogen:paraffin).

7. A process according to claim 1 in which the catalyst comprises a noble metal on the porous support.

8. A process according to claim 7 in which the noble metal comprises platinum.

9. A process according to claim 1 in which the crystalline phase material has a hexagonal arrangement of uniformly-sized pores with diameters of at least about 13 Å and exhibits, after calcination, a hexagonal electron diffraction pattern that can be indexed with a d_{100} value greater than about 18 Å.

10. A process according to claim 1 in which the crystalline phase has a composition expressed as follows:

$$M_{n/q}(W_aX_bY_cZ_dO_h)$$

wherein M is one or more ions; n is the charge of the composition excluding M expressed as oxides; q is the weighted molar average valence of M; n/q is the number of moles or mole fraction of M; W is one or more divalent elements; X is one or more trivalent elements; Y is one or more tetravalent elements; Z is one or more pentavalent elements; a, b, c, and d are mole fractions of W, X, Y, and Z, respectively; h is a number of from 1 to 2.5; and (a+b+c+d) = 1.

11. A process according to claim 10 wherein W comprises a divalent first row transition metal or magnesium; X comprises aluminum, boron, gallium or iron; Y comprises silicon or germanium; and Z comprises phosphorus.

12. A process according to claim 10 wherein a and d are 0 and h = 2.

13. A process according to claim 12 wherein X comprises aluminum and Y comprises silicon.

14. A process according to claim 1 in which the catalyst includes a component having Lewis acid or Bronsted acid activity.

15. A process according to claim 14 in which the catalyst includes aluminum trichloride or boron trifluoride.

FIG. 1

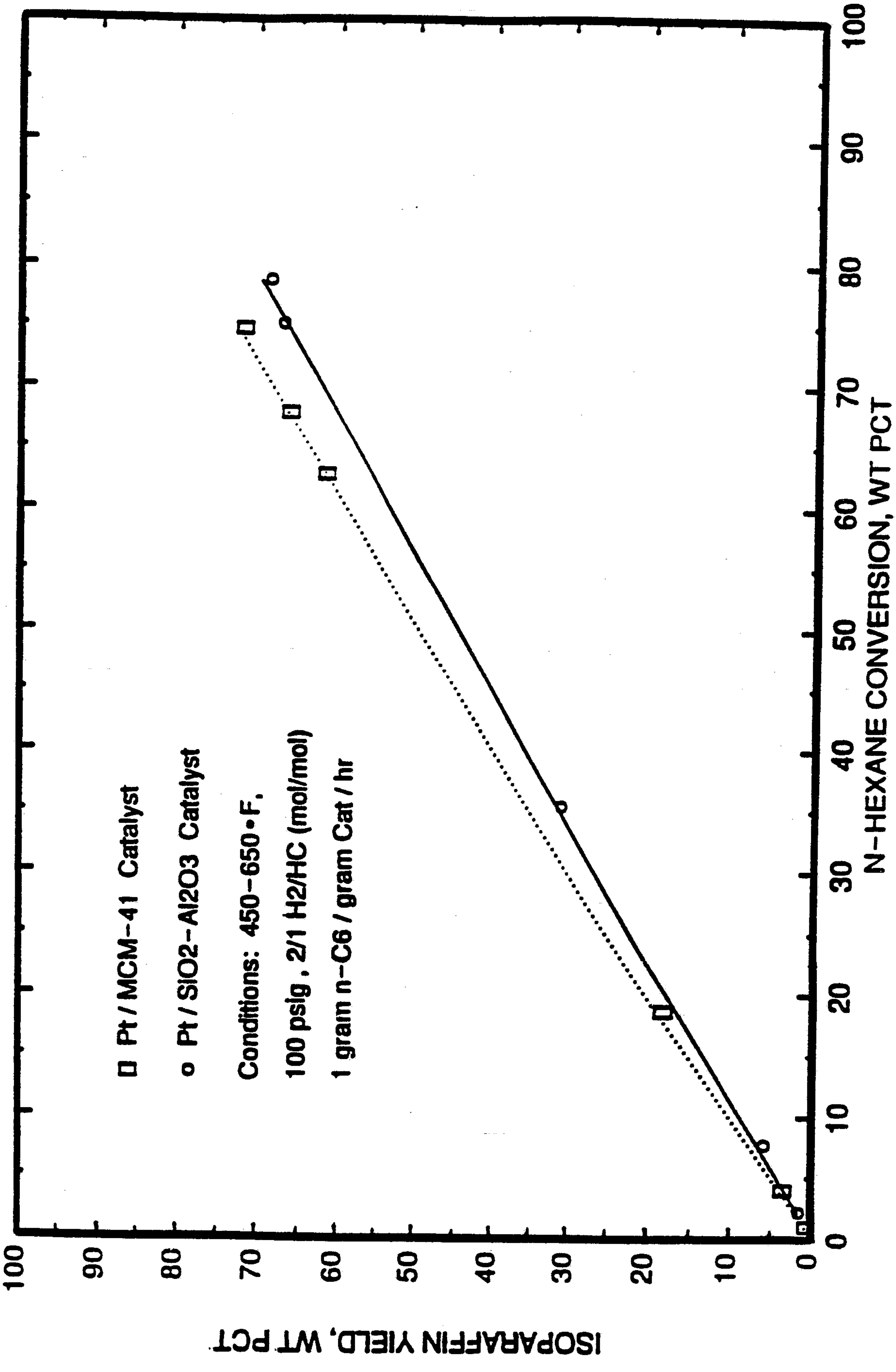
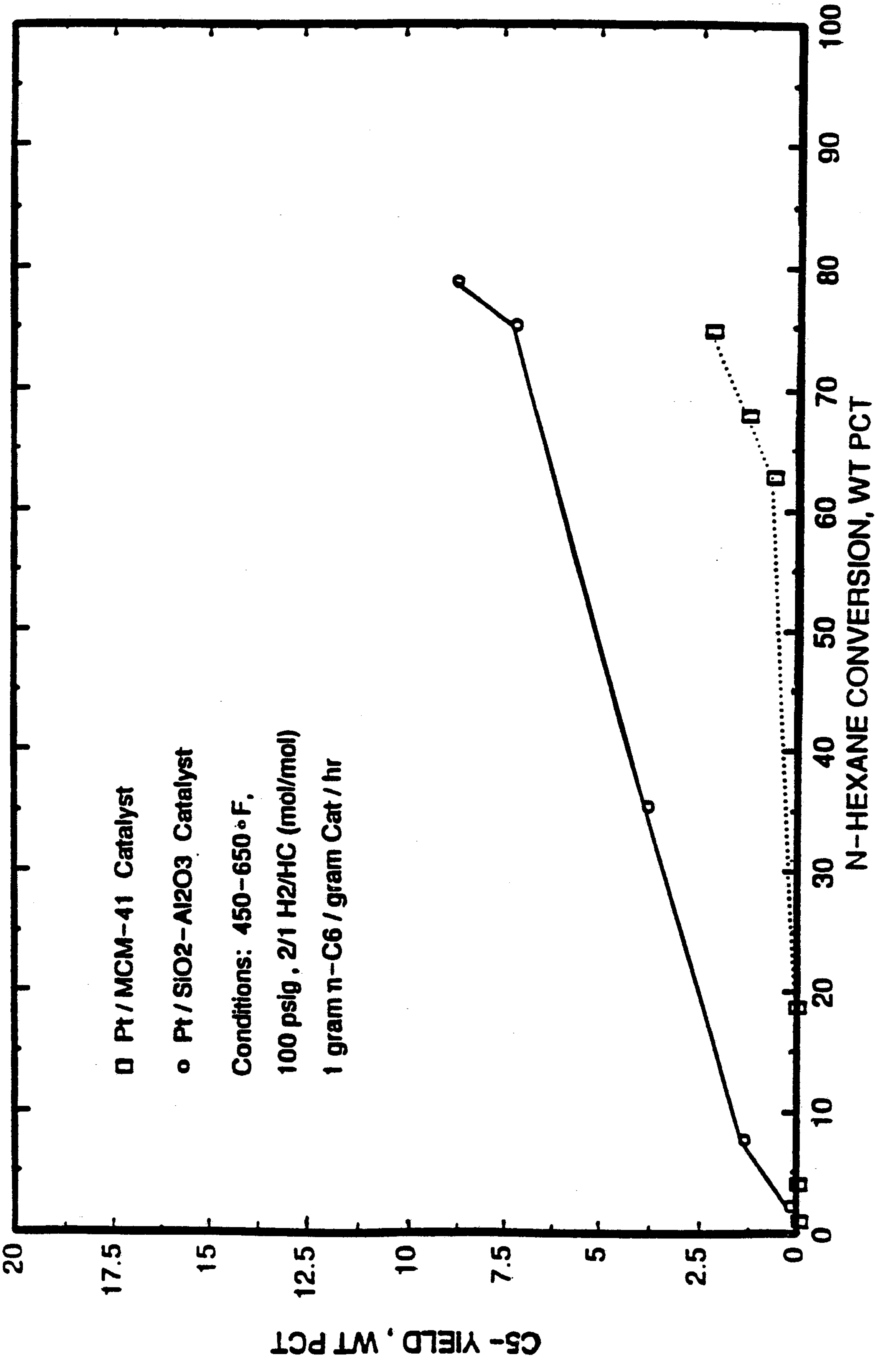

□ Pt / MCM-41 Catalyst
○ Pt / SiO2-Al2O3 Catalyst
Conditions: 450-650 • F,
100 psig , 2/1 H2/HC (mol/mol)
1 gram n-C6 / gram Cat / hr
N-HEXANE CONVERSION, WT PCT
0
10
20
30
40
50
60
70
80
90
100
ISOPARAFFIN YIELD, WT PCT
0
10
20
30
40
50
60
70
80
90
100

FIG. 2


□ Pt / MCM-41 Catalyst
○ Pt / SiO2-Al2O3 Catalyst
Conditions: 450-650 °F,
100 psig , 2/1 H2/HC (mol/mol)
1 gram n-C6 / gram Cat / hr
C5- YIELD , WT PCT
0
2.5
5
7.5
10
12.5
15
17.5
20
N-HEXANE CONVERSION, WT PCT
0
10
20
30
40
50
60
70
80
90
100

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/06099

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C10G 35/06; C07C 5/13
US CL :208/138; 585/739,744
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/138; 585/739,744

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; PARAFFIN, isomerization, catalyst

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US,A, 5,102,643 (KRESGE ET AL.), 07 APRIL 1992, See col. 3, lines 47-58; col. 4, lines 1-55; col. 6, lines 17-23; col. 8, lines 66-68.	1-15
Y	US,A, 4,778,944 (ZARCHY), 18 OCTOBER 1988, See col.2, lines 52-68; col. 3 lines 1-7,22-28, 42-48,65-68; col. 4, lines 1-17.	1-15
Y	US,A, 3,720,628 (HAYES ET AL.), 13 MARCH 1973, See col. 4, lines 39-44; col.6, lines 19-39; col. 9 lines 1-20.	14-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 04 SEPTEMBER 1992	Date of mailing of the international search report 14 DEC 1992
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