# United States Patent (19)

# Chu

# (54) ALKALINE EARTH METAL MODIFIED ZEOLITE CATALYSTS

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## Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 128,688, Mar. 10, 1980, Pat. No. 4,288,647.
- 51) int. Cl. .. B01J 29/28
- 52 U.S. C. ... 252/455 Z.
- 58) Field of Search .................................... 252/455 Z

# 56) References Cited

#### U.S. PATENT DOCUMENTS



# $[11]$  4,357,264

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## FOREIGN PATENT DOCUMENTS



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# [57] **ABSTRACT**

A zeolite catalyst composition suitable for para-selec tive conversion of substituted aromatic compounds, e.g., to dialkylbenzene compounds rich in the 1,4-dial kylbenzene isomer. Such a composition comprises a zeolite catalyst having a silica to alumina mole ratio of at least 12 and a constraint index of about 1-12, and a minor amount, e.g., at least 0.25 weight percent of one or more of the alkaline-earth metals (Ca, Sr, Ba), and optionally phosphorus.

## 12 Claims, No Drawings

# ALKALINE EARTH METAL MODIFIED ZEOLITE **CATALYSTS**

# BACKGROUND OF THE INVENTION CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of the appli cation of CHIN-CHIUN CHU having Ser. No. 128,688,  $_{10}$ <br>  $5! \times 10^{-10}$   $_{200}$  name U.S. Ret. No. 1290.647 filed Mar. 10, 1980 now U.S. Pat. No. 4,288,647.

# FIELD OF THE INVENTION

The invention disclosed herein relates to novel zeolite catalyst compositions which are particularly useful for the production of dialkylbenzene compound product mixtures in which the 1,4-dialkylbenzene isomer is sub stantially in excess of its normal equilibrium concentra tion. 15

#### DESCRIPTION OF THE PRIOR ART

The disproportionation of aromatic hydrocarbons in the presence of zeolite catalysts has been described by Grandio et al. in the OIL AND GAS JOURNAL, Vol. 69, Number 48(1971).

U.S. Pat. Nos. 3, 126,422; 3,413,374; 3,598,878; 3,598,879 and 3,607,961 show vapor-phase dispropor tionation of toluene over various catalysts. In these prior art processes, the dimethylbenzene U.S. Pat. Nos. 3,126,422; 3,413,374; 3,598,878; <sup>25</sup>

product produced has the equilibrium composition of approximately 24 percent of 1,4-, 54 percent of 1,3- and 22 percent of i,2-isomer. Of the dimethylbenzene iso mers, 1,3-dimethylbenzene is normally the least desired product, with 1,2- and 1,4-dimethylbenzene being the more useful products. 1,4-Dimethylbenzene is of partic thalic acid which is an intermediate in the manufacture of synthetic fibers such as "Dacron'. Mixtures of di methylbenzene isomers, either alone or in further admixture with ethylbenzene, have previously been separated by expensive superfractionation and multistage <sup>40</sup><br>refrigeration steps. Such process, as will be realized,<br>involves high operation costs and has a limited yield. ular value, being useful in the manufacture of tereph. 35 zene from toluene and methanol and 1-ethyl-4-methyl-

Various modified zeolite catalysts have been devel-<br>oped to alkylate or disproportionate toluene with a greater or lesser degree of selectivity to 1,4-dimethyl- <sup>45</sup> benzene isomer. Hence, U.S. Patents 3,972,832,<br>4,034,053, 4,128,592 and 4,137,195 disclose particular zeolite catalysts which have been treated with compounds of phosphorus and/or magnesium. Boron-containing zeolites are shown in U.S. Pat. No. 4.067.920 50 and antimony-containing zeolites in U.S. Pat. No. 3,979,472. Similarly, U.S. Pat. Nos. 3,965,208 and 4,117,026 disclose other modified zeolites useful for shape selective reactions. A number of prior art refer ences disclose the incorporation of various metal ions 55 into zeolite catalysts by means of ion exchange.

While the above-noted prior art is considered of interest in connection with the subject matter of the present invention, the crystalline zeolite catalysts of specified characteristics which have undergone the particu-60 lar treatment disclosed herein, have not, insofar as is known, been previously described.

#### SUMMARY OF THE INVENTION

In accordance with the present invention, there have 65 now been discovered novel alkaline earth metal modi fied zeolite catalyst compositions useful for conversion of organic compounds (e.g. hydrocarbon compounds).

An especially advantageous reaction promoted by the catalysts of this invention comprises the selective pro duction of the 1,4-isoner of dialkylated benzene com pounds. The process involves contacting an alkylated aromatic compound, either alone or in admixture with a with the particular type of modified crystalline zeolite catalyst disclosed herein and under suitable conversion tion of alkylbenzene compounds or alkylation of aromatic compounds to selectively produce the 1,4-dialkyl benzene isomer in excess of its normal equilibrium con centration.

20 use by initial treatment with a compound derived from The particular type of crystalline zeolite catalysts utilized herein are zeolite materials having a silica to alumina ratio of at least about 12 and a constraint index line zeolite compositions are modified prior to catalytic one or more of the elements comprising the alkaline earth metals (i.e. Ca, Sr and Ba) to yield a composite containing a minor proportion of an oxide of such element. In addition to treatment of the catalyst with the calcium, strontium or barium containing compound, the phorus-containing compound to deposit a minor proportion of an oxide of phosphorus thereon in addition to the oxide of the alkaline-earth metal.

Such catalysts can be employed for the alkylation of aromatic compounds to realize selective production of the 1,4-dialkylbenzene isomer in preference to the 1,2-<br>and 1,3- isomers thereof. Especially preferred processes involve the selective production of 1,4-dimethylben-

benzene from toluene and ethylene.<br>Such catalysts can also be employed to realize the<br>selective disproportionation or transalkylation of alkylbenzene and polyalkylbenzene compounds in the presence of the disclosed catalysts, thereby yielding 1,4-<br>disubstituted benzenes in excess of their normal equilibrium concentration. For example, under appropriate conditions of temperature and pressure, toluene will disproportionate in the presence of these catalysts to produce benzene and dimethylbenzenes rich in the de sirable 1,4-isomer.

# DESCRIPTION OF SPECIFIC EMBOOMENTS

The crystalline zeolites of the present invention are members of a novel class of zeolitic materials which exhibit unusual properties. Although these zeolites have unusually low alumina contents, i.e. high silica to alu mina mole ratios, they are very active even when the silica to alumina mole ratio exceeds 30. The activity is surprising, since catalytic activity is generally attributed to framework aluminum atoms and/or cations associ ated with these aluminum atoms. These zeolites retain their crystallinity for long periods in spite of the pres ence of steam at high temperature which induces irreversible collapse of the framework of other zeolites, e.g. of the X and A type. Furthermore, carbonaceous deposits, when formed, may be removed by burning at higher than usual temperatures to restore activity. These zeolites, used as catalysts, generally have low coke-forming activity and therefore as conducive to long times on stream between regenerations by burning carbonaceous deposits with oxygen-containing gas such as air.

An important characteristic of the crystal structure of this novel class of zeolites is that it provides a selective line free space by virtue of having an effective pore size intermediate between the small pore Linde A and the large pore Linde X, i.e. the pore windows of the struc ture are of about a size such as would be provided by 10-membered rings of silicon atoms interconnected by oxygen atoms. It is to be understood, of course, that of the tetrahedra making up the anionic framework of the crystalline zeolite, the oxygen atoms themselves being bonded to the silicon (or aluminum, etc.) atoms at the centers of the tetrahedra. these rings are those formed by the regular disposition 10

The silica to alumina mole ratio referred to may be 15 determined by conventional analysis. This ratio is meant to represent, as closely as possible, the ratio in the rigid anionic framework of the zeolite crystal and to exclude aluminum in the binder or in cationic or other form within the channels. Although zeolites with a silica to 20 alumina mole ratio of at least 12 are useful, it is pre ferred in some instances to use zeolites having substan tially higher silica/alumina ratios, e.g. 1600 and above. In addition, zeolites as otherwise characterized herein but which are substantially free of aluminum, that is 25 zeolites having silica to alumina mole ratios of up to infinity, are found to be useful and even preferable in some instances. Such "high silica" or "highly siliceous" zeolites are intended to be included within this descripzeolites are intended to be included within this descrip-<br>tion. Also to be included within this definition are sub- 30 stantially pure silica analogs of the useful zeolites de scribed herein, that is to say those zeolites having no measurable amount of aluminum (silica to alumina mole ratio of infinity) but which otherwise embody the char acteristics disclosed. 35

The novel class of zeolites, after activation, acquire an intracrystalline sorption capacity for normal hexane which is greater than that for water, i.e. they exhibit "hydrophobic" properties. This hydrophobic character can be used to advantage in some applications.

The novel class of zeolites useful herein have an ef fective pore size such as to freely sorb normal hexane. In addition, the structure must provide constrained access to larger molecules. It is sometimes possible to judge from a known crystal structure whether such 45 constrained access exists. For example, if the only pore windows in a crystal are formed by 8-membered rings of silicon and aluminum atoms, then access by mole cules of larger cross-section than normal hexane is ex cluded and the zeolite is not of the desired type. Win-50 dows of 10-membered rings are preferred, although in some instances excessive puckering of the rings or pore blockage may render these zeolites ineffective.

Although 12-membered rings in theory would not conversions, it is noted that the puckered 12-ring structure of TMA offretite does show some constrained access. Other 12-ring structures may exist which may be operative for other reasons and, therefore, it is not the present intention to entirely judge the usefulness of a 60 tant and even critical definition of those zeolites which particular zeolite solely from theoretical structure con siderations. offer sufficient constraint to produce advantageous 55

Rather than attempt to judge from crystal structure whether or not a zeolite possesses the necessary con strained access to molecules of larger cross-section than 65 normal paraffins, a simple determination of the "Constraint Index" as herein defined may be made by passing continuously a mixture of an equal weight of normal

hexane and 3-methylpentane over a sample of zeolite at atmospheric pressure according to the following proce dure. A sample of the zeolite, in the form of pellets or extrudate, is crushed to a particle size about that of coarse sand and mounted in a glass tube. Prior to test ing, the zeolite is treated with a stream of air at 540°C. for at least 15 minutes. The Zeolite is then flushed with helium and the temperature is adjusted between 290° C. and 510° C. to give an overall conversion of between 10% and 60%. The mixture of hydrocarbons is passed at 1 liquid hourly space velocity (i.e., 1 volume of liquid hydrocarbon per volume of zeolite per hour) over the zeolite with a helium dilution to give a helium to (total) hydrocarbon mole ratio of 4:1. After 20 minutes on stream, a sample of the effluent is taken and analyzed, most conveniently by gas chromatography, to determine the fraction remaining unchanged for each of the two hydrocarbons.

While the above experimental procedure will enable one to achieve the desired overall conversion of 10 to 60% for most zeolite samples and represents preferred conditions, it may occasionally be necessary to use low activity, such as those having an exceptionally high silica to alumina mole ratio. In those instances, a tem perature of up to about 540° C. and a liquid hourly space velocity of less than one, such as 0.1 or less, can be employed in order to achieve a minimum total conver sion of about 10%.

The "Constraint Index' is calculated as follows:

Constraint Index  $=$ 

log<sub>10</sub> (fraction of hexane remaining) log10 (fraction of 3-methylpentane remaining)

The Constraint Index approximates the ratio of the cracking rate constants for the two hydrocarbons. Zeo lites suitable for the present invention are those having a Constraint Index of 1 to 12. Constraint Index (CI) values for some typical materials are:



The above-described Constraint Index is an impor are useful in the instant invention. The very nature of this parameter and the recited technique by which it is determined, however, admit of the possibility that a given zeolite can be tested under somewhat different conditions and thereby exhibit different Constraint Indi ces. Constraint Index seems to vary somewhat with severity of operation (conversion) and the presence of absence of binders. Likewise, other variables such as

crystal size of the zeolite, the presence of occiuded contaminants, etc., may affect the constraint index. Therefore, it will be appreciated that it may be possible to so select test conditions as to establish more than one value in the range of 1 to 12 for the Constraint Index of a particular zeolite. Such a zeolite exhibits the con strained access as herein defined and is to be regarded as having a Constraint Index in the range of 1 to 12. Also contemplated herein as having a Constraint Index in the range of 1 to 12 and therefore within the scope of the  $10$ defined novel class of highly siliceous zeolites are those zeolites which, when tested under two or more sets of conditions within the above-specified ranges of temperature and conversion, produce a value of the Constraint index slightly less than 1, e.g. 0.9, or somewhat greater than 12, e.g. 14 or 15, with at least one other value within the range of 1 to 12. Thus, it should be under stood that the Constraint Index value as used herein is an inclusive rather than a exclusive value. That is, a crystalline zeolite when identified by any combination of conditions within the testing definition set forth herein as having a Constraint index in the range of 1 to 12 is intended to be included in the instant novel zeolite definition whether or not the same identical zeolite, 25 when tested under other of the defined conditions, may give a Constraint Index value outside of the range of 1 to 12.

I he novel class of zeolites defined herein is exempli-<br>fied by ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, 30 ZSM-38, 2SM-48 and other similar materials.

ZSM-5 is described in greater detail in U.S. Pat. Nos. 3,702,886 and Re 29,948. The entire descriptions con tained within those patents, particularly the X-ray dif  $\mu$  action pattern of therein disclosed  $\lambda$ SM-5, are incor-35 porated herein by reference.

ZSM-1 1 is described in U.S. Pat. No. 3,709,979. That description, and in particular the X-ray diffraction pat tern of said ZSM-11, is incorporated herein by reference.

ZSM-12 is described in U.S. Pat. No. 3,832,449. That description, and in particular the X-ray diffraction pat tern disclosed therein, is incorporated herein by reference.

 $2\text{SM-23}$  is described in U.S. Pat. No. 4,076,842. The  $45$ entire content thereof, particularly the specification of the X-ray diffraction pattern of the disclosed zeolite, is incorporated herein by reference.

 $\mu$   $\sim$  25 M-35 is described in U.S. Pat. No. 4,016,245. The  $\sim$  50 Section of that zeolite, and particularly the Y ray  $^{50}$ description of that zeolite, and particularly the X-ray diffraction pattern thereof, is incorporated herein by reference.

ZSM-38 is more particularly described in U.S. Pat. ticularly the specified X-ray diffraction pattern thereof,<br>is incorporated herein by reference.<br>ZSM-48 can be identified, in terms of moles of anhy-

drous oxides per 100 moles of silica, as follows:

 $(0-15)$  RN:  $(0-1.5)$   $M_{2/n}$ O:  $(0-2)$  Al<sub>2</sub>O<sub>3</sub>:  $(100)$ SiO<sub>2</sub> wherein:

M is at least one cation having a valence n; and

RN is a  $C_1$ -C<sub>20</sub> organic compound having at least one amine functional group of  $pKa \ge 7$ .

It is recognized that, particularly when the composi-  $65$ tion contains tetrahedral, framework aluminum, a fraction of the amine functional groups may be protonated. The doubly protonated form, in conventional notation,

wouid be (RNH)2O and is equivalent in stoichiometry to  $2RN + H<sub>2</sub>O$ .

5 The characteristic X-ray diffraction pattern of the synthetic zeolite ZSM-48 has the following significant lines:



20 per, and a scintillation counter spectrometer with a strip These values were determined by standard tech niques. The radiation was the K-alpha doublet of cop chart pen recorder was used. The peak heights, I, and the positions as a function of 2 times theta, where theta is the Bragg angle, were read from the spectrometer chart. From these, the relative intensities, 100  $I/I_o$ , where  $I_o$  is the intensity of the strongest line or peak, and d (obs.), the interplanar spacing in A, corresponding to the recorded lines, were calculated. in the fore going table the relative intensities are given in terms of the symbols  $W = weak$ ,  $VS = very$  strong and W- $S =$  weak-to-st rong. Ion exchange of the sodium with cations reveals substantially the same pattern with some minor shifts in interplanar spacing and variation in relative intensity. Other minor variations can occur depending on the silicon to aluminum ratio of the particular sample, as well as if it has been subjected to thermal treatment.

40 tion mixture should have a composition, in terms of The ZSM-48 can be prepared from a reaction mixture containing a source of silica, water, RN, an alkali metal oxide (e.g. sodium) and optionally alumina. The reac mole ratios of oxides, falling within the following ranges:



55 60 num. Thus aluminum sulfate, for example, would be wherein RN is a  $C_1-C_{20}$  organic compound having an amine functional group of  $pKa$  > 7. The mixture is maintained at 80°-250° C. until crystals of the material are formed.  $H^+$ (added) is moles acid added in excess of the moles of hydroxide added. In calculating  $H<sup>+</sup>$  (added) and OH values, the term acid  $(H<sup>+</sup>)$  includes both hydronium ion, whether free or coordinated, and alumiconsidered a mixture of aluminum oxide, sulfuric acid, and water. An amine hydrochloride would be a mixture of amine and HCl. In preparing the highly siliceous form of ZSM-48 no alumina is added. Thus, the only aluminum present occurs as an impurity in the reactants.

Preferably, crystallization is carried out under pres sure in an autoclave or static bomb reactor, at 80° C, to 250 C. Thereafter, the crystals are separated from the

liquid and recovered. The composition can be prepared utilizing materials which supply the appropriate oxide.<br>Such compositions include sodium silicate, silica hydrosol, silica gel, silicic acid, RN, sodium hydroxide, sodium chloride, aluminum sulfate, sodium aluminate, aluminum oxide, or aluminum itself. RN is a  $C_1-C_{20}$ organic compound containing at least one amine func tional group of  $pka > 7$ , as defined above, and includes such compounds as  $C_3-C_{18}$  primary, secondary, and tertiary amines, cyclic amine (such as piperidine, pyr-10<br>rolidine and piperazine), and polyamines such as NH<sub>2</sub>- $C_nH_{2n}$ -NH<sub>2</sub> wherein n is 4-12.

In all of the foregoing zeolites, the original cations can be subsequently replaced, at least in part, by calci nation and/or ion exchange with another cation. Thus, <sup>15</sup><br>the original cations can be exchanged into a hydrogen or hydrogen ion precursor form or a form in which the original cations have been replaced by a metal of, for example, Groups II through VIII of the Periodic Table. Thus, it is contemplated to exchange the original cati ons with ammonium ions or with hydronium ions. Cata-<br>lytically active forms of these would include, in particular, hydrogen, rare earth metals, aluminum, manganese and other metals of Groups II and VIII of the Periodic Table. 20 25

It is to be understood that by incorporating by reference the foregoing patents to describe examples of specific members of the novel class with greater particularity, it is intended that identification of the therein dis closed crystalline zeolites be resolved on the basis of their respective X-ray diffraction patterns. As discussed above, the present invention contemplates utilization of such catalysts wherein the mole ratio of silica to alu mina is essentially unbounded. The incorporation of the  $_{35}$ identified patents should therefore not be construed as limiting the disclosed crystalline zeolites to those hav ing the specific silica-alumina mole ratios discussed therein, it now being known that such zeolites may be substantially aluminum-free and yet, having the same <sub>40</sub> crystal structure as the disclosed materials, may be use ful or even preferred in some applications. It is the crystal structure, as identified by the X-ray diffraction, "fingerprint", which establishes the identity of the specific crystalline zeolite material. 30 45

The specific zeolites described, when prepared in the presence of organic cations, are substantially catalyti cally inactive, possibly because the intra-crystalline free space is occupied by organic cations from the forming solution. They may be activated by heating in an inert 50 atmosphere at 540° C. for one hour, for example, followed by base exchange with ammonium salts followed<br>by calcination at 540° C. in air. The presence of organic cations in the forming solution may not be absolutely the presence of these cations does appear to favor the formation of this special class of zeolite. More generally, it is desirable to activate this type catalyst by base exchange with ammonium salts followed by calcination in air at about  $540^\circ$  C. for from about 15 minutes to 60 about 24 hours. essential to the formation of this type zeolite; however, 55

Natural zeolites may sometimes be converted to zeo lite structures of the class herein identified by various activation procedures and other treatments such as base exchange, steaming, alumina extraction and calcination, 65 alone or in combinations. Natural minerals which may be so treated include ferrierite, brewsterite, stilbite, dachiardite, epistilbite, heulandite, and clinoptilolite.

The preferred crystalline zeolites for utilization herein include ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48, with ZSM-5 being par ticularly preferred.

In a preferred aspect of this invention, the zeolites hereof are selected as those providing among other things a crystal framework density, in the dry hydrogen form, of not less than about 1.6 grams per cubic centi meter. It has been found that zeolites which satisfy all three of the discussed criteria are most desired for sev eral reasons. When hydrocarbon products or by-pro-<br>ducts are catalytically formed, for example, such zeolites tend to maximize the production of gasoline boiling range hydrocarbon products. Therefore, the preferred zeolites useful with respect to this invention are those having a Constraint Index as defined above of about 1 to about 12, a silica to alumina mole ratio of at least about 12 and a dried crystal density of not less than about 1.6 grams per cubic centimeter. The dry density for known structures may be calculated from the number of silicon plus aluminum atoms per 1000 cubic Angstrons, as given, e.g., on Page 19 of the article ZEOLITE STRUCTURE by W. M. Meier. This paper, the entire contents of which are incorporated herein by reference, is included in PROCEEDINGS OF THE CONFER-ENCE ON MOLECULAR SIEVES, (London, April 1967) published by the Society of Chemical Industry, London, 1968.<br>When the crystal structure is unknown, the crystal

framework density may be determined by classical pyknometer techniques. For example, it may be determined by immersing the dry hydrogen form of the zeolite in an organic solvent which is not sorbed by the crystal. Or, the crystal density may be determined by mercury porosimetry, since mercury will fill the interstices between crystals but will not penetrate the intracrystalline free space.

It is possible that the unusual sustained activity and stability of this special class of zeolites is associated with its high crystal anionic framework density of not less density must necessarily be associated with a relatively small amount of free space within the crystal, which might be expected to result in more stable structures. This free space, however, is important as the locus of

catalytic activity.<br>Crystal framework densities of some typical zeolites, including some which are not within the purview of this invention, are:





When synthesized in the alkali metal form, the zeolite is conveniently converted to the hydrogen form, gener ally by intermediate formation of the ammonium form as a result of ammonium ion exchange and calcination 10 of the ammonium form to yield the hydrogen form. In addition to the hydrogen form, other forms of the Zeo lite wherein the original alkali metal has been reduced to less than about 1.5 percent by weight may be used as precursors to the alkaline-earth metal modified zeolites 15 of the present invention. Thus, the original alkali metal of the zeolite may be replaced by ion exchange with other suitable metal cations of Groups I through VIII of nickel, copper, zinc, palladium, calcium or rare earth metals. As discussed more fully hereinafter, incorporation of metal by ion exchange can contribute to the modification of the zeolites herein with the alkaline earth metals.

In practicing any given desired hydrocarbon conver- $25$ sion process, it may be useful to incorporate the above-<br>described crystalline zeolites with a matrix comprising another material resistant to the temperature and other conditions employed in the process. Such matrix mate rial is useful as a binder and imparts greater resistance to the catalyst for the severe temperature, pressure and reactant feed stream velocity conditions encountered in, for example, many cracking processes. 30

Useful matrix materials include both synthetic and  $35$ naturally occurring substances, as well as inorganic materials such as clay, silica and/or metal oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Naturally occurring clays which  $40<sub>1</sub>$ can be composited with the zeolite include those of the montmorillonite and kaolin families, which families<br>include the sub-bentonites and the kaolins commonly known as Dixie, McNamee-Georgia and Florida clays or others in which the main mineral constituent is hal- $45$ loysite, kaolinite, dickite, nacrite or anauxite. Such clays can be used in the raw state as originally mined or ini tially subjected to calcination, acid treatment or chemi cal modification.

In addition to the foregoing materials, the zeolites  $50$ employed herein may be composited with a porous matrix material, such as alumina, silica-alumina, silica and silica-titania, as well as ternary compositions, such alumina-magnesia and silica-magnesia-zirconia. The matrix may be in the form of a cogel. The relative proportions of zeolite component and inorganic oxide gel matrix, on an anhydrous basis, may vary widely with the zeolite content ranging from between about 1 to 60 about 99 percent by weight and more usually in the range of about 5 to about 80 percent by weight of the dry composite. as silica-alumina-thoria, silica-alumina-zirconia, silica- 55

The zeolite catalyst compositions as described herein are modified in accordance with the present invention 65 by incorporating thereon a minor amount of one or more of the alkaline-earth metals, said elements being calcium (Ca), strontium (Sr), and barium (Ba).

These alkaline-earth metals, as well as other optional components described hereinafter, are generally incor porated by contacting the zeolite composition with a solution containing one or more compounds of the ele ments to be incorporated. Incorporation can occur by the mechanisms of ion exchange, adsorption and/or impregnation, the latter two phenomena commonly being referred to as "stuffing." It should be emphasized that, while ion exchange can be used to incorporate the alkaline-earth or other metals onto the zeolite compositions described herein, ion exchange alone will generally not provide the requisite amount of incorporated alkaline-earth metal onto the zeolite catalyst compositions of the present invention. Combinations of incorporation element by stuffing.

rated may be formulated from any suitable solvent Solutions of compounds of such metals to be incorpo which is inert with respect to the metal-containing compound and the zeolite composition. Nonlimiting exam ples of some suitable solvents include water, aromatic and aliphatic hydrocarbons, alcohols, organic acids (such as acetic acid, formic acid, propionic acid and so forth), and inorganic acids (such as hydrochloric acid, sulfuric acid and nitric acid). Other commonly available solvents such as halogenated hydrocarbons, ketones, ethers, etc., may also be useful to dissolve some metal compounds or complexes. Generally, the most useful solvent will be found to be water. However, the solvent of choice for any particular compound will, of course, be determined by the nature of that compound and for that reason the foregoing list should not be considered exhaustive of all of the suitable possibilities. Representative calcium-containing compounds

which are useful for incorporating calcium onto the zeolite composition of the present invention include calcium acetate, calcium butyrate, calcium carbonate, calcium chloride, calcium bromide, calcium fluoride, calcium iodide, calcium chlorate, calcium citrate, cal cium cinnamate, calcium laurate, calcium maleate, cal cium nitrate, calcium nitrite, calcium oxide, calcium propionate, and calcium sulfide. This listing is not to be taken as encompassing all of the utilizable calcium con taining compounds. It is merely intended to be illustrative of some of the representative metal compounds which those in the art will find useful in practicing the disclosed invention. The knowledgeable reader will readily appreciate that there are numerous other known calcium salts and complexes which would prove useful herein to provide solutions containing calcium suitable for combination with the zeolite composition in the manner hereinafter described.<br>Reaction of the zeolite composition with the treating

calcium compound is effected by contacting the zeolite composition with such compound. Where the treating compound is a liquid, such compound can be as noted in solution in a solvent at the time contact with the zeolite composition is effected. Any solvent relatively inert with respect to the treating calcium compound and the zeolite may be employed. Suitable solvents for calcium compounds include water and aliphatic, aromatic or alcoholic liquids. The treating compound may also be used without a solvent, i.e. may be used as a neat liquid. Where the treating compound is in the gaseous phase, it can be used by itself or in admixture with a gaseous diluent relatively inert to the treating compound and

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the zeolite (such as helium or nitrogen) or with an or-<br>ganic solvent such as octane or toluene.

Heating of the calcium compound containing catalyst composition subsequent to preparation and prior to use is preferred, and such heating can be carried out in the presence of oxygen, for example, in air. Although heat ing may be carried out at a temperature of about 150° C., higher temperatures, e.g. up to about 500° C., are preferred. Heating is generally carried out for 1-5 hours but may be extended to 24 hours or longer. While heat- 10 ing temperatures above about  $500^{\circ}$  C. may be employed, they are generally not necessary. After heating in air at elevated temperatures, and without being limited by any theoretical considerations, it is contem plated that the calcium is actually present in the zeolite 15 composite in an oxidized state, such as CaO.

The amount of calcium incorporated in the zeolite composition is generally at least about 0.25 percent by weight. However, it is preferred that the amount be at least about 0.5 percent by weight, particularly when the 20 zeolite component is combined with a binder, e.g., 35 weight percent of alumina. The amount of calcium can be as high as about 30 percent by weight or more, depending on the amount and type of binder present. pending on the amount and type of binder present. Preferably, the amount of calcium added to the zeolite 25 composition will be between about 1 and about 20 per

The amount of calcium incorporated onto the zeolite composition by reaction with elemental calcium or composition by reaction with elemental calcium or calcium-containing compound will depend upon sev 30 eral factors. One of these is the reaction time, i.e., the time that the zeolite composition and the calcium-con taining source are maintained in contact with each other. With greater reaction times, all other factors being equal, a greater amount of metal is incorporated 35 with the zeolite. Other factors upon which the amount of calcium incorporated with the zeolite is dependent include reaction temperature, concentration of the treating compound in the reaction mixture, the degree to which the zeolite composition has been dried prior to reaction with the metal-containing compound, the con ditions of drying of the zeolite composition after reac tion with the treating compound, and the amount and type of binder incorporated with the zeolite composi tion. 45

Strontium and especially oxides of strontium, are also effective modifying components for imparting the desir able shape selective activity to the particular type of zeolite compositions disclosed. Examples of representazeolite compositions disclosed. Examples of representa-<br>tive strontium-containing compounds suitable for depo- 50 sition of that metal on the zeolite include strontium acetate, strontium bromide, strontium carbonate, stron tium chloride, strontium fluoride, strontium iodide, strontium formate, strontium chlorate, strontium lac tate, strontium nitrate, strontium nitrite, strontium ox 55 ide, strontium hyponitrite, strontium salicylate, stron tium sulfide, and strontium dithionate. As discussed above with respect to the illustrative listing of calcium compounds, the foregoing is not to be considered as an exhaustive list of the utilizable strontium salts and com- 60 plexes. There are numerous strontium compounds which the foregoing will suggest to those skilled in the art as being suitable for providing the strontium-con taining solutions for treatment of the zeolite composi-<br>tions as hereinafter described.<br>Reaction of the zeolite compositions with the stron-

tium compounds is accomplished in substantially the same way as that recited above with respect to the calcium-containing compounds. Without being limited by any theoretical considerations, it is contemplated that the strontium is likewise in an oxidized state, such as SrO.

The amount of strontium incorporated in the zeolite composition is generally at least about 0.25 percent by weight. However, it is preferred that the amount be at least about 1 percent by weight, particularly when the zeolite is combined with a binder, e.g. 35 weight percent of alumina. The amount of strontium can be as high as about 40 percent by weight or more depending on the amount and type of binder present. Preferably, the will be between about 1 and about 30 percent by weight.

Barium, and especially oxides of barium may also be employed as a modifying component. The barium oxide is contemplated as being present as BaO alone or in combination with other compounds of barium in an oxidized state. In all instances, regardless of the particu lar state of oxidation of the bariun, its content with respect to the zeolite composite is computed as if it were present as elemental barium. Generally, the amount of barium in the composite catalyst will be between about 0.25 and about 50 weight percent, and preferably be tween about 1 and about 45 weight percent, based on the weight of the composite. Reaction of the zeolite composition with the barium-containing compound is carried out as described above with respect to the treat ment with compounds of the element calcium. Exam ples of barium compounds which may be utilized in clude barium acetate, barium bromide, barium carbon ate, barium chloride, barium fluoride, barium iodide, barium cyanide, barium dithionate, barium formate, barium nitrate, barium nitrite, barium oxide, barium propionate and barium sulfide. Again, this listing is not intended to be exhaustive, but rather suggestive to those of skill in the art as to the kinds of metal-containing compounds useful for treating the zeolite compositions as herein described.

In some instances, it may be desirable to modify the crystalline zeolites by combining therewith two or more of the specified metal oxides. Thus, the zeolite composition may be modified by prior combination therewith of oxides of calcium and strontium, oxides of calcium and barium, oxides of strontium and barium, or even oxides of all three elements. When such modification technique is employed, the respective oxides may be deposited on the zeolite composite either sequentially or from a solution containing suitable compounds of the elements, the oxides of which are to be combined with the zeolite composition. The amounts of oxides present in such instance are in the same range as specified above for the individual oxides, with the overall added oxide content being between about 1 and about 50 weight percent of the composite, calculated on the basis of elemental alkaline earth metal content.

65 amount of phosphorus will be between about 1.0 weight A further embodiment of this invention includes addi tional modification of the above metal oxide - zeolite composites with phosphorus, whereby from about 0.25 weight percent to about 30 weight percent of an oxide of phosphorus, calculated as elemental phosphorus is combined with the zeolite composition. The preferred percent and about 25 weight percent phosphorus, based on the weight of the treated zeolite composite. The phosphorus treatment of the zeolite catalyst will prefer

ably be carried out before the previously described modification with the alkaline-earth metals. Reaction of the zeolite composition with the phosphorus-containing compound is carried out essentially as described above with respect to the metal-containing compounds and it 5 is preferred that the total amount of oxides combined with the zeolite, i.e. the phosphorus oxides plus the metal oxides, fall within the approximate range of 2 percent to 40 percent by weight, based on the weight of the treated zeolite compositions and calculated on the 10 basis of elemental phosphorus plus elemental alkaline earth metal.<br>Representative phosphorus-containing compounds

which may be used include derivatives of groups represented by PA3,  $KPA2$ ,  $K2PA$ ,  $K3P$ ,  $X3PO$ ,  $(XO)3PO$ , 15  $(XO)_{3}P$ ,  $R_{3}P=O$ ,  $R_{3}P=S$ ,  $RPO_{2}$ ,  $RPS_{2}$ ,  $RP(O)(OX)_{2}$ ,  $RP(S)(SX)_2$ ,  $R_2P(O)OX$ ,  $R_2P(S)SX$ ,  $RP(SX)_2$ ,  $ROP-(OX)_2$ ,  $RSP(SX)_2$ ,  $(RS)_2PSP(SR)_2$ , and  $(RO)_2POP-$ (OX)<sub>2</sub>, RSP(SX)<sub>2</sub>, (RS)<sub>2</sub>PSP(SR)<sub>2</sub>, and (RO)<sub>2</sub>POP-<br>(OR)<sub>2</sub>, where R is an alkyl or aryl, such as a phenyl radical and X is hydrogen, R, or halide. These com- 20 pounds include primary, RPH<sub>2</sub>, secondary, R<sub>2</sub>PH and tertiary,  $R_3P$ , phosphines such as butyl phosphine; the tertiary phosphine oxides  $R_3PO$ , such as tributylphosphine oxide, the tertiary phosphine sulfides,  $R_3PS$ , the phosphonic acids such as benzene phosphonic acid; the corresponding sulfur derivatives such as  $RP(S)(SX)_2$ and  $R_2P(S)SX$ , the esters of the phosphonic acids such as diethyl phosphonate,  $(RO)_2P(O)H$ , dialkyl alkyl as diethyl phosphonate, (RO)<sub>2</sub>P(O)H, dialkyl alkyl<br>phosphonates, (RO)<sub>2</sub>P(O)R, and alkyl dialkylphosphi- 30 nates, (RO)P(O)R2; phosphinous acids, R2POX, such as diethylphosphinous acid, primary, (RO)P(OX)2, sec ondary, (RO)<sub>2</sub>POX, and tertiary, (RO)<sub>3</sub>P, phosphites; and esters thereof such as the monopropyl ester, alkyl and esters thereor such as the monopropyl ester, alkyl<br>dialkylphosphinites, (RO)PR<sub>2</sub>, and dialkyl alkylphos-<br>phinite, (RO)<sub>2</sub>PR esters. Corresponding sulfur derivatives may also be employed including  $(RS)_2P(S)H$ ,  $(RS)P(S)R_2$ ,  $R_2PSX$ ,  $(RS)P(SX)_2$ , (RS)<sub>2</sub>PSX, (RS)<sub>3</sub>P, (RS)PR<sub>2</sub> and (RS)<sub>2</sub>PR. Examples of phosphite esters include trimethylphosphite, triethylphosphite, diisopropylphosphite, butylphosphite, and pyrophosphites such as tetraethylpyrophosphite. The alkyl groups in the mentioned compounds contain from one to four carbon atoms. primary, RP(O)(OX)<sub>2</sub>, and secondary, R<sub>2</sub>P(O)OX, 25 phosphite esters include trimethylphosphite, triethyl- 40

include the phosphorus halides such as phosphorus<br>trichloride, bromide, and iodide, alkyl phosphorodi-<br>chloridites, (RO)PCl<sub>2</sub>, dialkyl phosphorochloridites,<br>(RO)<sub>2</sub>PCl, dialkylphosphinochloridites, R<sub>2</sub>PCl, alkyl<br>alkylph alkylphosphonochloridates, (RO)(R)P(O)Cl, dialkyl 50 any mono- or di-substituted benzenes which are alkyla-

Preferred phosphorus-containing compounds include diphenyl phosphine chloride, trimethylphosphite and 55 phosphorus trichloride, phosphoric acid, phenyl phosphine oxychloride, trimethylphosphate, diphenyl phosphinic acid, diethylchlorothiophosphate, methyl acid phosphate and other alcohol-P<sub>2</sub>O<sub>5</sub> reaction products.

Particularly preferred are ammonium phosphates, including ammonium hydrogen phosphate, (NH4)<sub>2</sub>HPO<sub>4</sub>, and ammonium dihydrogen phosphate, NH4H<sub>2</sub>PO<sub>4</sub>.

Still another optional modifying treatment entails 65 steaming of the zeolite composite by contact with an atmosphere containing from about 5 to about 100 per cent steam at a temperature of from about 250° to about

1000° C. for a period of between about 15 minutes and about 100 hours and under pressures ranging from sub atmospheric to several hundred atmospheres. Prefera bly, steam treatment is effected at a temperature of between about 400° C. and about 700° C. for a period of

between about 1 and about 24 hours.<br>Another optional modifying treatment involves precoking of the catalyst to deposit a coating of between about 2 and about 75, and preferably between about 15 ing can be accomplished by contacting the catalyst with<br>a hydrocarbon charge, e.g. toluene, under high severity conditions or alternatively at a reduced hydrogen to hydrocarbon concentration, i.e. 0 to 1 mole ratio of hydrogen to hydrocarbon, for a sufficient time to de

posit the desired amount of coke thereon.<br>It is also contemplated that a combination of steaming and precoking of the catalyst under the above conditions may be employed to suitably modify the crystal-

35 Alkylation of aromatic compounds in the presence of the above-described catalyst is effected by contact of the aromatic with an alkylating agent. A particularly preferred embodiment involves the alkylation of toluene wherein the alkylating agents employed comprise methanol or other well known methylating agents or ethylene. The reaction is carried out at a temperature of between about 250° C. and about 750° C., preferably between about 300 $^{\circ}$  C. and 650 $^{\circ}$  C. At higher temperatures, the zeolites of high silica/alumina ratio are preferred. For example, ZSM-5 having a  $SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>$  ratio of 30 and upwards is exceptionally stable at high tem peratures. The reaction generally takes place at atmo spheric pressure, but pressures within the approximate range of  $10^5$  N/m<sup>2</sup> to  $10^7$  N/m<sup>2</sup> (1-100 atmospheres) may be employed.

Some non-limiting examples of suitable alkylating agents would include olefins such as, for example, ethyl ene, propylene, butene, decene and dodecene, as well as formaldehyde, alkyl halides and alcohols, the alkyl por tion thereof having from 1 to 16 carbon atoms. Numer ous other aliphatic compounds having at least one reac tive alkyl radical may be utilized as alkylating agents. Aromatic compounds which may be selectively al

Other suitable phosphorus-containing compounds 45 kylated as described herein would include any alkylatable aromatic hydrocarbon such as, for example, benzene, ethylbenzene, toluene, dimethylbenzene, diethylbenzene, methylethylbenzene, propylbenzene, isopropylbenzene, isopropylmethylbenzene, or substantially

table in the 4-position of the aromatic ring.<br>The molar ratio of alkylating agent to aromatic compound is generally between about 0.05 and about 5. For ing agent and toluene is the aromatic, a suitable molar ratio of methanol to toluene has been found to be approximately 1-0.1 mole of methanol per mole of toluene. Reaction is suitably accomplished utilizing a feed weight hourly space velocity (WHSV) of between 60 about 1 and about 1000, and preferably between about 1 and about 200. The reaction product, consisting predominantly of the 1,4-dialkyl isomer, e.g. 1,4-dimethyl-<br>benzene, 1-ethyl-4-methylbenzene, etc., or a mixture of<br>the 1,4- and 1,2- isomers together with comparatively smaller amounts of 1,3-dialkylbenzene isomer, may be separated by any suitable means. Such means may in clude, for example, passing the reaction product stream through a water condenser and subsequently passing

the organic phase through a column in which chro matographic separation of the aromatic isomers is ac complished.

When transalkylation is to be accomplished, transalk-<br>vlating agents are alkyl or polyalkyl aromatic hydrocarbons wherein alkyl may be composed of from 1 to about 5 carbon atoms, such as, for example, toluene, xylene, trimethylbenzene, triethylbenzene, dimethylethylbenzene, ethylbenzene, diethylbenzene, ethyltoluene, and so forth.

Another reaction involving catalysts of this invention<br>relates to the selective disproportionation of alkylated aromatic compounds to produce dialkylbenzenes wherein the yield of 1,4-dialkyl isomer is in excess of the normal equilibrium concentration. In this context, it 15 should be noted that disproportionation is a special case<br>of transalkylation in which the alkylatable hydrocarbon and the transalkylating agent are the same compound, for example when toluene serves as the donor and ac ceptor of a transferred methyl group to produce ben- $_{20}$ zene and xylene. The transalkylation and disproportionation reactions

are carried out by contacting the reactants with the above described modified zeolite catalyst at a tempera of between atmospheric ( $10^5$  N/m<sup>2</sup>) and about 100 atmospheres (107 N/m<sup>2</sup>). The reactant feed WHSV will normally fall within the range of about 0.1 to about 50. Preferred alkylated aromatic compounds suitable for utilization in the disproportionation embodiment com- $_{30}$ prise toluene, ethylbenzene, propylbenzene or substan tially any mono-substituted alkylbenzene. These aromatic compounds are selectively converted to, respecmatic compounds are selectively converted to, respec-<br>tively, 1,4-dimethylbenzene, 1,4-diethylbenzene, 1,4-<br>dipropylbenzene, or other 1,4-dialkylbenzene, as appro-<br>priate, with benzene being a primary side product in each instance. The product is recovered from the reac tor effluent by conventional means, such as distillation, to remove the desired products of benzene and dialkylbenzene, and any unreacted aromatic component is  $\mu$ recycled for further reaction. ture of between about 250° C. and 750° C. at a pressure  $2\pi$ 

The hydrocarbon conversion processes described herein may be carried out as a batch type, semi-continuous or continuous operation utilizing a fixed or moving ous or continuous operation utilizing a fixed or moving<br>bed catalyst system. The catalyst after use in a moving 45<br>hed recotor is conducted to a reconomistion regal bed reactor is conducted to a regeneration zone<br>wherein coke is burned from the catalyst in an oxygencontaining atmosphere, e.g. air, at an elevated temperature, after which the regenerated catalyst is recycled to stock. In a fixed bed reactor, regeneration is carried out in a conventional manner where an inert gas containing a small amount of oxygen (0.5-2%) is used to burn the coke in a controlled manner so as to limit the tempera ture to a maximum of around 500°-550° C. the conversion zone for further contact with the charge  $50$ 

The following examples will serve to illustrate cer tain specific embodiments of the hereindisclosed inven tion. These examples should not, however, be construed as limiting the scope of the novel invention, as there are many variations which may be made thereon without departing from the spirit of the disclosed invention, as those of skill in the art will recognize.

#### EXAMPLE 1A

#### Alkylation reaction with unmodified ZSM-5

Five grams of HZSM-5 (silica/alumina mole ration-70; 65% on alumina binder) were placed in a quartz flow reactor and heated to various temperatures between 350° C. and 500° C. A mixture of toluene and methanol, at a 4/1 molar ratio, was passed thru the zeolite catalyst at a weight hourly space velocity (WHSV) of 10. The reactor effluent was monitored and the results obtained at the various temperatures are shown below.



#### EXAMPLE. 1B

In a similar manner, toluene was alkylated with ethyl ene by passing toluene and ethylene, at WHSV of 7.0 and 0.5, respectively, over the unmodified zeolite. The results at various temperatures are shown below.



#### EXAMPLE 2

Disproportionation reaction with unmodified ZSM-5)

Toluene was passed over a 6.0 g sample of HZSM-5  $(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>$  mole ratio = 70; 65% on alumina binder) at a feed WHSV of 3.5-3.6 and at temperatures between 450° C. and 600° C. The results are summarized below.



#### EXAMPLE 3

#### Preparation of Ca-modified zeolite)

55 Six grams of HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio=70) were mixed with a solution of  $6.0 \text{ g Ca}(\text{NO}_3)_2.4\text{H}_2\text{O}$  in 10 ml water at  $80^{\circ}$  C. The mixture was maintained at about  $80^{\circ}$  C. for 2 hours. The zeolite was removed by filtration, dried at 90° C. overnight, and then calcined at 500 C. for 3 hours to yield 6.53 g Ca-ZSM-5. Analysis indicated a calcium content of 5.58%.

### EXAMPLE 4

#### Alkylation reaction with Ca-modified zeolite

65 modified zeolite at WHSV of 7.0 and 0.5, respectively, Five grams of the Ca-ZSM-5 zeolite of Example 3 were placed in a flow reactor and heated to 400° C. A feed stream of toluene and ethylene was passed over the and the reactor effluent analyzed. Toluene conversion was 29.4% and the yield of para-isomer in the ethyltol uene product 70.3%. This represents a dramatic in

crease in selectivity to the para-isomer relative to the equilibrium concentration of approximately 30% achieved with the unmodified zeolite (Example 1B).

#### EXAMPLE 5

Disproportionation reaction with Ca-modified zeolitel

Disproportionation of toluene was carried out by passing toluene over a 5.0 g sample of the Ca-ZSM-5 zeolite of Example 3. The feed WHSV was  $3.5$  and the  $_{10}$ temperature of the reactor was 550° C. Toluene conver sion was 1.8% with 29.9% para-xylene in the xylene product. By comparison, the unmodified ZSM-5 dem onstrated only about 24% selectivity to para-xylene under the same reaction conditions (Example 2). 15

#### EXAMPLE 6

#### Preparation of Sr-modified zeolite)

A solution of 5.0 g Sr(OAc)<sub>2</sub> in 15 ml H<sub>2</sub>O was prepared and heated to 80° C. Added 5.0 g of HZSM-5  $(SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>$  mole ratio=70) and maintained the mixture at 80°-90° C. for 2 hours. After filtering and drying at 90° C. for 2 hours, the zeolite was calcined at 500 C. to yield 5.52 g of Sr-ZSM-5. The content of strontium  $_{25}$  was found to be 10.7%. 20

#### EXAMPLE 7A

Alkylation reaction with Sr-modified zeolite)

Alkylation of toluene with methanol was carried out <sup>30</sup> by passing a toluene/methanol mixture (molar rati o=4/1) over 4.0 g of the Sr-ZSM-5 zeolite of Example 6 at  $400^{\circ}$  C. and feed WHSV = 10. Toluene conversion was 30% with 60.6% para-isomer in the xylene product. tivity relative to the unmodified ZSM-5 (Example 1A). This is a two-and-one-half-fold increase in para-selec- 35

#### EXAMPLE 7B

In a similar manner, toluene was ethylated by passing  $\frac{40}{2}$ a toluene/ethylene feed stream (WHSV =  $7.0$  and 0.5, respectively) over the Sr-ZSM-5 zeolite at 400° C. Conversion of toluene was 47.5% and the yield of para-iso-<br>mer in the ethyltoluene was 64.5%. Again, there is a mer in the ethyltoluene was 64.5%. Again, there is a very substantial and surprising increase in para-selec-<br>tivity over that attained by the unmodified zeolite (Ex-<br>ample 1B).

#### EXAMPLE 8

 $\mu_{\text{S}}$  Disproportionation reaction with Sr-modified zeolite  $\mu_{\text{S}}$ 

A toluene feed stream was passed over the Sr-ZSM-5 zeolite of Example 6 to study the toluene diproportiona tion reaction. The toluene WHSV was 3.5 and the reac tor was at 550° C. Toluene conversion was 1.5% and the para-isomer in the xylene product was 31.2%. This <sup>55</sup> compares very favorably with the 24.2% selectivity of the unmodified ZSM-5 (Example 2).

# EXAMPLE 9

#### Preparaion of Ba-modified zeolite)

Dissolved 5.0 g Ba(OAc)<sub>2</sub> in 7.0 ml H<sub>2</sub>O at 80 $^{\circ}$  C, and added 3.0 g HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio = 70). The mixture was maintained at 80°-90° C. for 3 hours then the zeolite was recovered by filtration and dried at  $65$ about 90° C. for 1.5 hours. The dried zeolite was then calcined to yield 3.57 g Ba-ZSM-5. The barium content was found to be 15.4%.

# EXAMPLE 10A

## Alkylation reaction with Ba-modified zeolite)

Alkylation of toluene with methanol in the presence of the Ba-modified zeolite catalyst was carried out by passing a feed stream of toluene and methanol (molar ratio=4/1) over a 1.1 g sample of the Ba-ZSM-5 zeolite of Example 9 at 500° C. The reactor effluent was analyzed and toluene conversion was found to be 26.0% with 53.6% para-isomer in the xylene produced. The unmodified zeolite, under identical conditions, gave only 24.2% of the paraisomer (Example 1A).

#### EXAMPLE 10B

In a similar manner, toluene was ethylated by passing toluene (WHSV=7.0) and ethylene (WHSV=0.5) over the Ba-ZSM-5 zeolite of Example 9 at 400° C. Conversion of toluene was 5.5% and the yield of para-isomer in the ethyltoluene product was found to be 80.7%. The paraselectivity for the unmodified ZSM-5 was only 29.9% (Example 1B).

# EXAMPLE 11

### Disoproportionation reaction with Ba-modified zeolite)

Toluene was disproportionated to xylenes by passing<br>a feed stream of toluene over the Ba-ZSM-5 of Example 9 at WHSV of 3.5 and 550° C. Toluene conversion was produced. Once again, a very substantial improvement relative to the unmodified zeolite (Example 2) was shown.

#### EXAMPLE 12

#### Preparation of P-modified zeolite

Two hundred grams of ammonium-ZSM-5 (65% on alumina binder) were added to a solution of 80 g of diammonium hydrogen phosphate in 300 ml of H2O at about 90° C. After standing at about 90° C. for 2 hours, the zeolite was filtered, dried at 90° C. for 2 hours and then calcined at 500° C. for another 2 hours. The recovered P-ZSM-5 zeolite contained 3.43 wt % phosphorus.

# EXAMPLE 13A

#### Alkyltion reaction with P-modified zeolite

Alkylation of toluene with methanol was carried out<br>by passing a toluene/methanol feed stream (molar ratiby passing a toluene/methanol feed stream (molar rati-12. The feed WHSV was 10 and the reactor temperature was varied between 400° C. and 600° C. The results obtained are summarized beiow.



#### EXAMPLE 13B

In a similar manner, ethylation of toluene was accomplished utilizing a feed stream of toluene (WHSV =  $7.0$ ) and ethylene (WHSV=0.5) in the presence of the P-ZSM-5 catalyst at 400 C. Conversion of toluene was

60

60

74.8% and selectivity to the para-isomer of ethyltoluene was 55.5%.

# EXAMPLE 14

Disproportionation reaction with P-modified zeolite 5

Toluene diproportionation was tested by passing a stream of toluene over the P-ZSM-5 catalyst of Exam ple 12 at a feed WHSV of 3.5 and at temperatures of rized below.



#### EXAMPLE 15

## Preparation of Ca-P-modified zeolite)

Six grams of the P-modified ZSM-5 zeolite prepared<br>in Example 12 were mixed with a solution of 6.0 g Ca- 25 (OAc)2.H2O in 15 ml H2O at about 90° C. The mixture was maintained at 80°-90° C. for 2 hours and then fil tered to recover the zeolite. The solid was dried at 90' C. overnight and then calcined for 2 hours to yield 6.91 g of Ca-P-ZSM-5. Analysis indicated the modified zeo-  $30$ lite contained 3.58% phosphorus and 6.03% calcium.

#### EXAMPLE 16A

Alkylation reaction with Ca-P-modified zeolite)

Alkylation of toluene with methanol was carried out by passing a toluene/methanol mixture (4/1 molar ra tio) over 5.0 g of the Ca-P-ZSM-5 zeolite of Example 15 at  $400^{\circ}$  C. and WHSV of 10. Toluene conversion was found to be  $40.8\%$  with a 91.5% selectivity to the para  $40$ isomer in the xylene product. Under similar conditions, the zeolite which had been modified with only phosphorus demonstrated 66.6% paraselectivity (Example 13A).

#### EXAMPLE 16B

Ethylation of toluene was accomplished by passing toluene and ethylene over the Ca-P-ZSM-5 catalyst at WHSV of 7.0 and 0.5, respectively. The catalyst temperature was maintained at 400° C. Conversion of tolu-50 ene was 95.8% and selectivity to para-ethyltoluene relative to the amount of ethytoluene produced was 91.4%. Once again, the modification of the zeolite as disclosed herein has brought about a tremendous im provement relative to both the unmodified and the <sup>55</sup> phosphorus modified zeolites.

#### EXAMPLE 17

## Disproportionation reaction with Ca-P modified zeolite

Toluene disproportionation was accomplished by passing a toluene feed stream over the Ca-P-ZSM-5 zeolite of Example 15 at 500° C. and WHSV of 3.5. Toluene conversion was 13.7% and selectivity to the 65 para isomer of xylene was 58.0%. Under the same con ditions, P-ZSM-5 showed only 35.1% para-selectivity (Example 14).

# EXAMPLE 18

# Preparation of Sr-P-modified zeolite)

between  $475^{\circ}$  C. and  $550^{\circ}$  C. The results are summa- 10 yield 6.45 g Sr-P-ZSM-5. Upon analysis the content of Six grams of the P-modified ZSM-5 zeolite from Example 12 were mixed with a solution of 5.0 g  $Sr(OAc)<sub>2</sub>$  in 15 ml of H<sub>2</sub>O. The mixture was maintained at 80°-90° C. for 2.3 hours. After filtration and drying at 90° C., the zeolite was calcined at 500° C. for 2 hours to phosphorus was found to be 3.18% and that of stron tium was 7.93%.

#### EXAMPLE 19A

#### Alkylation reaction with Sr-P modified zeolite)

20 tion temperature was 500 C. and the feed rate (WHSV) Toluene was alkylated with methanol by passing a toluene/methanol (molar ratio=4/1) feed stream over 5.0 g of the Sr-P-ZSM-5 zeolite of Example 18. Reac was 10. Toluene conversion was found to be 56.4% with an 84.5% selectivity to the para isomer in the xylene product.

### EXAMPLE 19B

Toluene was reacted with ethylene to produce ethyl toluene by passing a feed stream of toluene and ethylene (WHSV of 7.0 and 0.5, respectively) over 5.0 g of the Sr-P-ZSM-5 zeolite of Example 18 at 400° C. Conver sion of toluene was 70.9% with 92.3% selectivity to the para isomer in the ethyltoluene produced.

#### EXAMPLE 20

# Disproportionation reaction with Sr-P-modified zeolite

Disproportionation of toluene to xylenes was carried out by passing a feed stream of toluene over the Sr-Pmodified ZSM-5 zeolite of Example 18 at a WHSV of 3.5. The reaction was conducted at 500° C. Toluene conversion was 4.9% with 71.2%. para isomer in the xylene produced.

45 ment in para selectivity realized by modification of the Examples 19 and 20 clearly demonstrate the improve P-ZSM-5 zeolite with strontium.

#### EXAMPLE 21

# Preparation of Ba-P-modified zeolite

Added 6.0 g of the P-ZSM-5 zeolite prepared in Ex ample 12 to an 80° C. solution of 8.0 g Ba(OAc)2 in 15 ml of water. The mixture was maintained at 80°-90° C. for 2 hours then filtered and the zeolite dried at 90° C. overnight. After calcining at 500° C. for 2 hours, there were 8.30 g of Ba-P-ZSM-5 recovered. Analysis in dicarted the modified zeolite contained 2.78% phospho rus and 16.0% barium.

#### EXAMPLE 22

# Disproportionation reaction with Ba-P modified zeolite

Disproportionation of toluene to xylenes was carried out at  $500^{\circ}$  C. by contacting toluene (feed WHSV=3.5) with the Ba-P-ZSM-5 of Example 21. Toluene conver sion was 0.3% with 65% selectivity to para-xylene in xylenes.

# EXAMPLE 23

Disproportionation reaction with unmodified ZSM-11)

A 1.0 portion of unmodified HZSM-11 zeolite (silica A 1.0 portion of unmodified HZSM-11 zeolite (silica  $5$  to alumina mole ratio = 70) was placed in a quartz flow reactor and heated to temperature. Toluene was passed over the zeolite at WHSV of 3.8 and various tempera tures between 400° C. and 600° C. The results are summarized below.



#### EXAMPLE 24A

#### Alkylation reaction with umodified ZSM-11)

A toluene/methanol feed stream, having a 4/1 molar ratio of the respective reactants, was passed over un-  $25$ modified HZSM-11 zeolite  $(SiO_2/Al_2O_3=70)$  at 400°-600° C. and a feed WHSV of 10. The results are shown below.



#### EXAMPLE 24B

A toluene/ethylene feed stream was similarly brought into contact with the unmodified HZSM-11. The feed WHSV was 7.5 and 0.55, respectively, and the temperature of reaction 400°-450° C. The results are summarized below.



## EXAMPLE 25

## Preparation of Ba-modified ZSM-11

There are added 1.5 grams HZSM-11 zeolite (silica to alumina mole ratio=70) to a solution of 3.5 g barium acetate in 5.0 ml of water at 80° C. The mixture was maintained at  $80^{\circ}$ -90° C. for 2.5 hours, then filtered and<br>the reality dried at  $90^{\circ}$  C. cusmight, After arbitration of  $\frac{60}{2}$ the zeolite dried at 90° C. overnight. After calcining at 500° C., 2.30 g of Ba-ZSM-11 were recovered having an analyzed barium content of 40.6%.

#### EXAMPLE 26A

Alkylation reaction with Ba-modified ZSM-11

Alkylation of toluene with methanol was carried out at a feed WHSV of 10. Toluene conversion was 37.5% with 63.9% selectivity to the para isomer in the xylene produced.

# EXAMPLE 26B

Toluene and ethylene were reacted over the Ba modified ZSM-11 at 400° C. The feed WHSV for toluene was 7.0 and for ethylene was 0.5. Conversion of toluene was 5.3% and the yield of para-ethyltoluene in the ethyltoluene produced was 89.0%.

#### EXAMPLE 27

#### Disproportionation reaction with Ba-modified ZSM-11

15  $2<sub>0</sub>$ Disproportionation of toluene to xylenes in the pres ence of the Ba-ZSM-11 zeolite of Example 25 was car ried out by passing toluene over the modified zeolite at WHSV of 3.5 and a temperature of 600° C. Toluene conversion was 6.0% with 46.3% selectivity to para-<br>xylene.

It is to be understood that the foregoing is intended to be merely illustrative of certain specific embodiments of the disclosed invention. As those of skill in the art will readily appreciate, there are many variations which may be made on these specific embodiments without departing from the spirit of my invention and such variations are clearly to be encompassed within ambit of the following claims.

1. A catalyst composition suitable for para-selective conversion of substituted aromatic compounds, said 35 ther having incorporated thereon at least 0.25 weight What is claimed is:<br>1. A catalyst composition suitable for para-selective composition comprising a modified crystalline zeolite catalyst component characterized by a silica to alumina mole ratio of at least 12 and a constraint index within the approximate range of 1 to 12, said composition fur percent of at least one alkaline-earth metal selected from strontium and barium, said alkaline-earth metal being present in said catalyst in the form of its oxide.

40 strontium. 2. The composition of claim 1 wherein said element is

3. The composition of claim 2 wherein said strontium comprises between 1 and 30 weight percent of the mod ified zeolite catalyst composition.

45 barium. 4. The composition of claim 1 wherein said element is

5. The composition of claim 4 wherein said barium comprises between 1 and 45 weight percent of the mod ified zeolite catalyst composition.

6. The composition of claim 1 wherein said zeolite 0 catalyst composition has deposited thereon at least 0.25 weight percent of phosphorus in addition to said alka line-earth metal, said phosphorus also being present in said catalyst in the form of its oxide.

55 earth metal is strontium. 7. The composition of claim 6 wherein said alkaline

8. The composition of claim 6 wherein said alkaline earth metal is barium.

9. The composition of claim 1 wherein said zeolite is admixed with a binder therefor.

10. The composition of claim 1, 3, 5, 6 or 9 wherein said zeolite is selected from the group consisting of ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-38 and ZSM-48.

65 is ZSM-5. 11. The composition of claim 10 wherein said zeolite

12. The composition of claim 10 wherein said zeolite is  $ZSM-11$ .