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(54) Titre : COMPOSITION DE CATALYSEUR AMELIORE COMPRENANT LA ZEOLITE MCM-22
(54) Title: IMPROVED MCM-22 CATALYST COMPOSITION

(57) Abrégé/Abstract:

This invention relates to the catalyst composition resulting from the addition of phosphorus, and optionally, a matrix material, to a porous crystalline material having the structure of MCM-22. The addition of phosphorus to the MCM-22 is found to improve the hydrothermal stability of the resulting catalyst. The improved catalyst is useful in organic conversion processes, e.g., catalytic cracking processes.

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(54) Title: IMPROVED MCM-22 CATALYST COMPOSITION

(57) Abstract

This invention relates to the catalyst composition resulting from the addition of phosphorus, and optionally, a matrix material, to a porous crystalline material having the structure of MCM-22. The addition of phosphorus to the MCM-22 is found to improve the hydrothermal stability of the resulting catalyst. The improved catalyst is useful in organic conversion processes, e.g., catalytic cracking processes.

IMPROVED MCM-22 CATALYST COMPOSITION

This invention relates to an improved catalyst composition comprising the zeolite MCM-22.

MCM-22 is a known zeolite, whose characterising X-ray diffraction pattern and method of synthesis are described in U.S. Patent No. 4,954,325. In particular, MCM-22 has an X-ray diffraction pattern including the lines listed in Table 1, below:

TABLE 1

Interplanar d-Spacing (Å)	Relative Intensity, $I/I_o \times 100$
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06	VS

It is also known, see U.S. Patent Nos. 4,983,276 and 5,039,640, that MCM-22 is useful in catalytic cracking, such as fluid catalytic cracking (FCC), to increase the total gasoline yield and the octane number of the gasoline fraction.

It is desirable to improve the hydrothermal stability of MCM-22 containing catalysts particularly where the catalysts are subjected to repeated cycles of high temperature steaming such as is experienced in the FCC process.

In accordance with the present invention, there is provided an improved catalyst composition comprising phosphorus in combination with a zeolite having an X-ray diffraction pattern including the following lines:

Interplanar d-Spacing (Å)	Relative Intensity, I/I_o x 100
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06	VS

A matrix material may be included in the catalyst composition of this invention and the phosphorus may be added to either the porous crystalline material, the matrix material or both materials. Also the catalyst composition of this invention may be admixed with a large pore crystalline molecular sieve or mesoporous material. The improved catalyst of this invention may be used in organic conversion processes, such as catalytic cracking processes.

The catalyst composition of the present invention comprises the zeolite MCM-22 which, in its calcined form, has an X-ray diffraction pattern including the lines listed in Table 1 above. Generally, the calcined form of MCM-22 has an X-ray diffraction pattern including the following lines shown in Table 2 below:

TABLE 2

Interplanar d-Spacing (Å)	Relative Intensity, I/I_o x 100
30.0 ± 2.2	W-M
22.1 ± 1.3	W
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06	VS

More specifically, the calcined form of MCM-22 has an X-ray diffraction pattern including the following lines shown in Table 3 below:

TABLE 3

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

Most specifically, the calcined form of MCM-22 has an X-ray diffraction pattern including the following lines shown in Table 4 below:

TABLE 4

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

These values were determined by standard techniques. The radiation was the K-alpha doublet of copper and a diffractometer equipped with a scintillation counter and an associated computer was used. The peak heights, I, and the positions as a function of 2 theta, where theta is the

Bragg angle, were determined using algorithms on the computer associated with the diffractometer. 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 Angstrom Units (Å), corresponding to the recorded lines, were determined. In Tables 1-4, the relative intensities are given in terms of the symbols W = weak, M = medium, S = strong, VS = very strong. In terms of relative intensities, these may be generally designated as follows:

W = 0-20
M = 20-40
S = 40-60
VS = 60-100

Zeolite MCM-22 has a chemical composition expressed by the molar relationship:

$$X_2O_3:(n)YO_2,$$

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

$$(0.005\text{-}0.1)Na_2O:(1\text{-}4)R:X_2O_3:nYO_2$$

where R is an organic component. The Na and R components are associated with the zeolite as a result of their presence during crystallization, and are easily removed by conventional post-crystallization methods.

As is evident from the above formula, MCM-22 is synthesized nearly free of Na cations and thus possesses acid catalysis activity as synthesized. It can, therefore, be used as a component of the catalyst composition herein without having to first undergo an ion exchange step. To the extent desired, however, the original sodium cations of the as-synthesized material can be replaced at least in part by established techniques including ion exchange with other cations. Preferred replacement cations include metal ions, hydrogen ions, hydrogen precursor ions, e.g., ammonium and mixtures of such ions. Particularly preferred cations are those which tailor the activity of the catalyst for cracking. These include hydrogen, rare earth metals and metals of Groups IIA, IIIA, IVA, IB, IIB, IIIB, IVB, and VIII of the Periodic Table of the Elements.

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

Reactants	Useful	Preferred
YO_2/X_2O_3	10 - 60	10 - 40
H_2O/YO_2	5 - 100	10 - 50
OH^-/YO_2	0.01 - 1.0	0.1 - 0.5
M/YO_2	0.01 - 2.0	0.1 - 1.0
R/YO_2	0.05 - 1.0	0.1 - 0.5

The organic directing agent for use in synthesizing zeolite MCM-22 from the above reaction mixture is hexamethyleneimine.

In a preferred method of synthesizing zeolite MCM-22, the YO_2 reactant contains a substantial amount of solid YO_2, e.g., at least about 30 wt.% solid YO_2. Where YO_2 is silica, the use of a silica source containing at least about 30 wt.% solid silica, e.g., Ultrasil™ (a precipitated, spray dried silica containing about 90 wt.% silica) or HiSil™ (a precipitated hydrated SiO_2 containing about 87 wt.% silica, about 6 wt.% free H_2O and about 4.5 wt.% bound H2O of hydration and having a particle size of about 0.02

micron) favors crystal formation from the above mixture. If another source of oxide of silicon, e.g., Q-Brand (a sodium silicate comprised of about 28.8 wt.% of SiO_2, 8.9 wt.% Na_2O and 62.3 wt.% H_2O) is used, crystallization may yield impurity phases of other crystal structures, e.g., ZSM-12. Preferably, therefore, the YO_2, e.g., silica, source contains at least about 30 wt.% solid YO_2, e.g., silica, and more preferably at least about 40 wt.% solid YO_2, e.g., silica.

Crystallization of the MCM-22 crystalline material can be carried out at either static or stirred conditions in a suitable reactor vessel such as, e.g., polypropylene jars or teflon-lined or stainless steel autoclaves, at a temperature of 80°C to 225°C for 25 hours to 230 days, after which the crystals are separated from the liquid and recovered.

The present invention concerns a composition comprising a porous crystalline material characterized by an X-ray diffraction pattern including values substantially as set forth in Table 1 of the specification, said porous crystalline material having been contacted with a source of phosphorus. The composition may further comprise at least one matrix material, non-limiting examples of which include at least one of clay, alumina, silica and mixtures thereof. Either the porous crystalline material, the matrix material, or both may be contacted with the source of phosphorus.

One embodiment of the present invention is a method for manufacture of a composition comprising the steps of modifying a porous crystalline material characterized by an X-ray diffraction pattern including values substantially as set forth in Table 1 of the specification by contacting said porous crystalline material with a source of phosphorus and forming a catalyst particle from the phosphorus modified porous crystalline material.

Another embodiment of the present invention is a method for manufacture of a composition comprising the steps of combining a porous crystalline material characterized by an X-ray diffraction pattern including values substantially as set forth in Table 1 of the specification and a source of phosphorus and at least one of a source of clay, a source of silica, a source of alumina, and mixtures thereof, and forming catalyst particles from said combination.

A more specific embodiment of this invention is a method for manufacture of a composition comprising the steps of preparing a slurry of a porous crystalline material characterized by an X-ray diffraction pattern including values substantially as set forth in Table 1 of the specification, then blending a source of clay into the slurry, then adding a source of phosphorus to the slurry, then adding a source of silica and a source of alumina to the slurry, and finally forming catalyst particles from the slurry. The phosphorus may be added to any one or all of the slurries used to make the product. The phosphorus may also be added to the formed particle or to any particle used in the composition.

Non-limiting examples of the source of phosphorus useful in the present invention include ammonium monohydrogen phosphate, ammonium dihydrogen phosphate, triammonium phosphate, ammonium hypophosphate, ammonium orthophosphate, ammonium dihydrogen orthophosphate, ammonium monohydrogen orthophosphate, ammonium hypophosphite, ammonium dihydrogen orthophosphite, phosphoric acid and mixtures thereof, more specifically phosphoric acid and ammonium dihydrogen phosphate, and most specifically, phosphoric acid.

After treatment with the phosphorus source, but prior to use, the catalyst composition of the invention is preferably heated in the presence of oxygen, such as in air, typically at a temperature of 150 to 750°C. The phosphorus is typically added in an amount sufficient to yield a concentration of at least 0.1 wt.%, preferably 0.5 to 15wt%, on the finished catalyst. It will be appreciated that the phosphorus on the final catalyst will probably not be present in elemental form but rather as an oxide.

Non-limiting examples of the matrix material include clays and inorganic oxides. Naturally occurring clays which can be used as matrix material include the montmorillonite and kaolin family, which families include the subbentonites, and the kaolins commonly known as Dixie, McNamee, Georgia, and Florida clays or others in which the main mineral constituent is halloysite, kaolinite, dickite, nacrite, or anauxite. Inorganic oxides which can be used as the matrix material include silica, alumina, silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-berylia, silica-titania, as well as ternary oxide compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia-zirconia. The relative proportions of catalyst component(s) and matrix can vary widely with the content of the former ranging from 1 to 95, and more usually from 10 to 70, weight percent, of the composite.

Preferred examples of materials useful in this invention include kaolin clay as the source of clay, phosphoric acid or ammonium dihydrogen phosphate as the source of phosphorus, colloidal silica as the source of silica, and pseudoboehmite alumina as the source of alumina. Preferably, the catalyst should be formed and dried as rapidly as possible after mixing.

The composition of this invention may be useful in catalytic cracking, either alone, combined with a matrix, combined with a large pore crystalline molecular sieve, which is itself catalytically active, combined with a mesoporous material, or with combinations of the above.

The large pore (e.g., greater than about 7 Angstroms) crystalline molecular sieve which may be used is a material

normally having a Constraint Index (as defined in U.S. Patent No. 4,016,218)
less than 1. Large pore crystalline molecular sieves are well known in the art and include faujasite, mordenite, zeolite X, rare-earth exchanged zeolite X (REX), zeolite Y, zeolite Y (HY), rare earth-exchanged ultra stable zeolite Y (RE-USY), dealuminized Y (DAY), ultrahydrophobic zeolite Y (UHP-Y), dealuminized silicon enriched zeolites such as LZ-210, zeolite ZK-5, zeolite ZK-4, zeolite Beta, zeolite Omega, zeolite L, ZSM-20 and other natural or synthetic zeolites.

Other large pore crystalline molecular sieves which are useful herein include pillared silicates and/or clays; aluminophosphates, e.g., ALPO4-5, VPI-5; silicoalumino-phospates, e.g., MCM-9, SAPO-5, SAPO-37, SAPO-31, SAPO-40, SAPO-41; and other metal aluminophosphates. These materials are variously described in U.S. Patent Nos. 4,440,871; 4,554,143; 4,567,029; 4,666,875; 4,742,033.

The mesoporous materials useful in the present invention include crystals having uniform pores within the range of from about 13 Å to about 200 Å in diameter, more usually from about 15 Å to about 100 Å. Since these pores are significantly larger than those of other crystalline materials, it is also appropriate to refer to them as ultra-large pore size materials. For the purposes of this application, a working definition of "porous" is a material that absorbs at least 1 gram of a small molecule, such as Ar, N2, n-hexane, or cyclohexane, per 100 grams of solid. Non-limiting examples of mesoporous material are MCM-41 and MCM-48, which are substantially described in U.S. Patent Nos. 5,098,684; 5,102,643; 5,198,203. These mesoporous materials are useful in catalytic cracking processes as disclosed in U.S. Patent No. 5,232,580.

The amount of the porous crystalline material of Table 1 which is added to the large pore or mesoporous crystalline cracking catalyst component may vary from cracking unit to cracking unit depending upon the desired octane number, total gasoline yield required, the nature of the available feedstock and other similar factors. For many cracking operations, the weight percent of the porous crystalline material (e.g., MCM-22) relative to the total quantity of catalyst composition can range from 0.1 to 90 wt.%, specifically from 1 to 75 wt.%, more specifically from 2 to 50 wt.%., and most specifically from 4 to 25 wt.%.

Although the phosphorus-containing catalyst composition of the invention need not be steamed prior to use in a catalytic cracking process, and, in fact, will typically not be steamed prior to use therein, it may be steamed at a temperature of 300°C to 800°C for a time of 1 to 200 hours in 5 to 100 % steam.

As mentioned earlier, the catalyst composition of this invention is useful as a catalyst for organic compound, e.g., hydrocarbon compound, conversion. Non-limiting examples of processes for organic compound conversion include Fluid Catalytic Cracking (FCC) and other forms of catalytic cracking including moving bed catalytic cracking and hydrocracking.

Suitable catalytic cracking conditions include a temperature ranging from 370 to 700°C (700 to 1300°F) and a pressure ranging from subatmospheric to several hundreds of atmospheres. The catalytic cracking process can be either fixed bed, moving bed, transfer line, or fluidized bed, and the hydrocarbon flow may be either concurrent or countercurrent to the catalyst flow. The process of the invention is particularly applicable to the Fluid Catalytic Cracking (FCC) or Thermofor Catalytic Cracking (TCC) processes. In both of these processes, the hydrocarbon feed and catalyst are passed through a reactor and the catalyst is regenerated. The two processes differ substantially in the size of the catalyst particles and in the engineering contact and transfer which is at least partially a function of catalyst size.

The TCC process is a moving bed and the catalyst is in the shape of pellets or beads having an average particle size of about one-sixty-fourth to one-fourth inch. Active, hot catalyst beads progress downwardly cocurrent with a hydrocarbon charge stock through a cracking reaction zone. The hydrocarbon products are separated from the coked catalyst and recovered, and the catalyst is recovered at the lower end of the zone and regenerated.

Typical TCC conversion conditions include an average reactor temperature of 450°C to 540°C; catalyst/oil volume ratio of 2 to 7; reactor volume hourly space velocity of 1 to 5 vol./hr./vol.; and recycle to fresh feed ratio of from 0 to 0.5 (volume).

The process of the invention is also applicable to Fluid Catalytic Cracking (FCC). In fluidized catalytic cracking processes, the catalyst is a fine powder of 10 to 200 microns. This powder is generally suspended in the feed and propelled upward in a reaction zone. A relatively heavy hydrocarbon feedstock, e.g., a gas oil, is admixed with a suitable cracking catalyst to provide a fluidized suspension and cracked in an elongated reactor, or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The gaseous reaction products and spent catalyst are discharged from the riser into a separator, e.g., a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a product recovery zone and the spent catalyst entering a dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbons from the spent catalyst prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst bed where it desorbs such hydrocarbons conveying them to the product recovery zone. The fluidizable catalyst is continuously circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which is endothermic.

The FCC conversion conditions include a riser top temperature of 500°C to 595°C, specifically 520°C to 565°C, and most specifically 530°C to 550°C; catalyst/oil weight ratio of 3 to 12, specifically 4 to 11, and most specifically 5 to 10; and catalyst residence time of 0.5 to 15 seconds, specifically 1 to 10 seconds.

It is generally necessary that the catalysts be resistant to mechanical attrition, that is, the formation of fines which are small particles, e.g., less than 20 μm. The cycles of cracking and regeneration at high flow rates and temperatures, such as in an FCC process, have a tendency to break down the catalyst into fines, as compared with an average diameter of catalyst particles of 60-100 microns. In an FCC process, catalyst particles range from 10 to 200 microns, preferably from 20 to 150 microns. Excessive generation of catalyst fines increases the refiner's catalyst costs.

The feedstock, that is, the hydrocarbons to be cracked, may include in whole or in part, a gas oil (e.g., light, medium, or heavy gas oil) having an initial boiling point above about 204°C, a 50 % point of at least about 260°C, and an end point of at least about 315°C. The feedstock may also include deep cut gas oil, vacuum gas oil, thermal oil, residual oil, cycle stock, whole top crude, tar sand oil, shale oil, synthetic fuel, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, asphalts, hydrotreated feedstocks derived from any of the foregoing, and the like. As will be recognized, the distillation of higher boiling petroleum fractions above about 400°C must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein are expressed in terms of convenience of the boiling point corrected to atmospheric pressure. Resids or deeper cut gas oils having an end point of up to about 700°C, even with high metals contents, can also be cracked using the invention.

The invention will now be more particularly described with reference to the Examples and the accompanying drawing, which is a graph showing the effect of phosphorus addition on the alpha activity of MCM-22 catalysts exposed to steam at 540°C.

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

When ion-exchange capacity and temperature of the maximum rate of ammonia desorption are examined, they are determined by titrating, with a solution of sulfamic acid, the gaseous ammonia evolved during the temperature-programmed decomposition of the ammonium-form of the zeolite or its phosphorus incorporated form (TPAD). The basic method is described in Thermochimica Acta, Vol. III, pp. 113-124, 1971, by G. T. Kerr and A. W. Chester.

The 130.3 Mhz ^{27}Al nuclear magnetic resonance (NMR) quantitative data were obtained using 1.5 μs pulses with the solution 90°=9.0 μs and a 100 ms recycle. The method is similar to that described in Klinowski, J., Thomas, J.

M., Fyfe, C. A., Gobbi, G. C., and Hartman, J. S., Inorg. Chem., 22 (1983) 63.

Whenever sorption data are set forth for comparison of sorptive capacities for water, cyclohexane and/or n-hexane, they are Equilibrium Adsorption values determined as follows:

A weighed sample of the calcined adsorbent was contacted with the desired pure adsorbate vapor in an adsorbent chamber, evacuated to less than 1 mm Hg and contacted with 1.6 kPa (12 Torr) of water vapor or 5.3 kPa (40 Torr) of n-hexane or 5.3 kPa (40 Torr) of cyclohexane vapor, pressures less than the vapor-liquid equilibrium pressure of the respective adsorbate at 90°C. The pressure was kept constant (within about ± 0.5 mm Hg) by addition of adsorbate vapor controlled by a manostat during the adsorption period, which did not exceed about 8 hours. As adsorbate was adsorbed by the MCM-22 crystalline material, the decrease in pressure caused the manostat to open a valve which admitted more adsorbate vapor to the chamber to restore the above control pressures. Sorption was complete when the pressure change was not sufficient to activate the manostat. The increase in weight was calculated as the adsorption capacity of the sample in g/100 g of calcined adsorbent. Before phosphorus addition, zeolite MCM-22 exhibits equilibrium adsorption values than about 10 wt.% for water vapor, greater than about 4.5 wt.%, usually greater than about 7 wt.% for cyclohexane vapor and greater than about 10 wt.% for n-hexane vapor.

Catalysts of this invention were prepared and tested for attrition resistance as represented by an Attrition Index (AI). The Attrition Index is defined as the weight percentage of the fines generated during the test that are 20 microns or less in size relative to the amount of material larger than 20 microns present before the test. In the test, a 7 cc catalyst sample is contacted in a 1 inch (inside diameter) U-tube with an air jet formed by humidified (60%) air through an 0.07 inch nozzle at 21 liters per minute for one hour.

$$AI = 100 * \frac{\text{wt.\% fines AA} - \text{wt.\% fines BA}}{100 - \text{wt.\% fines BA}}$$

where BA is before attrition test and AA is after attrition test. The lower the Attrition Index, the more attrition resistant is the catalyst.

Example 1

MCM-22, synthesized according to U.S. Patent 4,954,325, was calcined at 480°C (900°F) in nitrogen for 3 hours and then in air at 540°C (1,000°F) for 9 hours. MCM-22 was then ammonium exchanged, dried at 250°F and air calcined at 1,000°F for 3 hours. The resulting catalyst is designated Catalyst A and has the following properties:

Phosphorus content, Wt.%	0
Alpha activity	280
TPAD	0.63 meq NH_3/g
Td $Al2O_3$, wt.%, ^{27}Al NMR	3.2

Example 2

A sample prepared similarly to that of Example 1 was contacted with an aqueous solution of ammonium dihydrogen phosphate to incorporate a nominal 1 wt.% phosphorus, dried at 120°C (250°F) and calcined in air at 540°C (1,000°F) for 3 hours. It was then steamed at 540°C (1,000°F) for 2.5 hours. The resulting catalyst is designated Catalyst B and has the following properties:

Phosphorus content, Wt.%	1
Alpha activity	154
TPAD	0.22 meq NH_3/g
Td $Al2O_3$, wt.%, ^{27}Al NMR	2.1

The catalyst of Example 2 showed a reduction of 45% in alpha activity, 65% in TPAD value, and 34% in ^{27}Al NMR value after steaming.

Example 3

A sample of the catalyst prepared in Example 1 above was steamed at 540°C (1,000°F) for 2.5 hours. The catalyst was not contacted with phosphorus before steaming. The resulting catalyst is designated Catalyst C and has the following properties:

Phosphorus content, Wt.%	0
Alpha activity	72
TPAD	0.15 meq NH$_3$/g
Td Al2O$_3$, wt.%, ^{27}Al NMR	1.6

The catalyst of Example 3 showed a decrease of 74% in alpha activity, 76% in TPAD, and 50% in ^{27}Al NMR value after steaming. Examples 2 and 3 show that incorporation of phosphorus improves retention of framework aluminum and, correspondingly cracking activity, in steamed catalysts.

Example 4

A phosphorus modified fluid catalyst containing 25 wt.% zeolite MCM-22 was prepared by first making a slurry of zeolite MCM-22, synthesized according to U.S. Patent 4,954,325. The zeolite slurry was prepared by calcining zeolite MCM-22 for 3 hours at 480°C (900°F) and then ballmilling the calcined zeolite for 16 hours at 25% solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse™ N-22, Reed-Lignin, Inc., Greenwich, CT). Kaolin clay (Kaopaque™ 10S, a Georgia kaolin clay, Dry Branch Chemical Co., Dry Branch, GA) was then blended into the zeolite slurry. To the zeolite and clay slurry, sufficient phosphoric acid (J. T. Baker Co., Phillipsburg, NJ) was added to result in a phosphorus level of 1.9 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica (Nalco™ 1034A, Nalco Chemical Co., Chicago, IL) and then alumina (Condea Pural™, SBIII pseudoboehmite alumina, Condea Chemie GMBH, Hamburg, Germany) peptized with formic acid. The matrix contains about 50 wt.% clay and about 50 wt.% binder and the binder contains about 5 parts by weight silica and about 1 part by weight alumina. The resulting slurry was spray dried (Niro Inc., Columbia, MD, spray dryer) at an outlet temperature of 180°C (360°F). The spray dried material was calcined for two hours at 540°C (1,000°F) in air. The resulting catalyst is designated Catalyst D and has the following properties:

Phosphorus content, Wt.%	1.9
Alpha activity	51

Example 5

A phosphorus modified fluid catalyst containing 25 wt.% zeolite MCM-22 was prepared by first making a slurry of zeolite MCM-22. The zeolite slurry was prepared by precalcining zeolite MCM-22 for 3 hours at 480°C (900°F) in nitrogen and then ballmilling the calcined zeolite for 16 hours at 25% solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse N-22). Kaolin clay (Kaopaque 10S, a Georgia kaolin clay) was then blended into the zeolite slurry. To the zeolite and clay slurry, sufficient ammonium dihydrogen phosphate (Sigma-Aldrich Corp., Milwaukee, WI) was added to result in a phosphorus level of 1.6 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica (Nalco 1034A) and then alumina (Condea Pural, SBIII pseudoboehmite alumina) peptized with formic acid. The matrix contains about 50 wt.% clay and about 50 wt.% binder composed of about 5 parts by weight silica and about 1 part by weight alumina. The resulting slurry was spray dried at an outlet temperature of 180°C (360°F). The spray dried material was calcined for two hours at 540°C (1,000°F) in air. The resulting catalyst is designated Catalyst E and has the following properties:

Phosphorus content, Wt.%	1.6
Alpha activity	50

Example 6

A catalyst compositionally similar to the catalysts prepared in Examples 4 and 5 was prepared without the use of phosphorus by mixing the silica-alumina binder (Nalco 1034A silica and Condea Pural SBIII pseudoboehmite alumina, peptized with formic acid), and subsequently adding the kaolin clay (Kaopaque 10S) and then the ballmilled zeolite slurry. The ballmilled zeolite slurry was prepared by precalcining zeolite MCM-22 for 3 hours at 480°C (900°F) in nitrogen and ballmilling the calcined zeolite for 16 hours at 25% solids with deionized water (DI) and 0.6 wt.% dispersant (Marasperse N-22). The matrix contains about 50 wt.% clay and about 50 wt.% binder compsed of about 5 parts by weight silica and about 1 part by weight alumina. The resulting slurry was spray dried at an outlet temperature of 180°C (360°F). The spray dried material was calcined for 2 hours in air at 540°C (1,000°F). The resulting catalyst is designated Catalyst F and has the following properties:

Phosphorus content, Wt.%	0
Alpha activity	72

A comparison of the properties of the catalysts of Examples 4, 5, and 6 shows that the incorporation of phosphorus into the catalyst composition initially decreases the alpha activity of the catalyst.

Example 7

Three identical samples of the calcined catalyst of Example 4 were treated in 100% steam at 540°C (1,000°F) at atmospheric pressure for either 2, 5, or 10 hours. These steam treated catalysts are designated Catalysts G, H, and I and have the following properties:

Catalyst Designation	Steaming Time, hrs	Phosphorus Content, wt.%	Alpha Activity
G	2	1.9	30
H	5	1.9	26
I	10	1.9	16

Example 8

Three identical samples of the calcined catalyst of Example 5 were treated in 100% steam at 540° (1,000°F) at atmospheric pressure for either 2, 5, or 10 hours. These steam treated catalysts are designated Catalysts J, K, and L and have the following properties:

Catalyst Designation	Steaming Time, hrs	Phosphorus Content, wt.%	Alpha Activity
J	2	1.6	29
K	5	1.6	26
L	10	1.6	17

A comparison of the alpha activities of the catalysts of Examples 7 and 8 shows that the incorporation of phosphorus into the catalyst via either phosphoric acid or ammonium dihydrogen phosphate results in a similar response of alpha as a function of steaming time.

Example 9

Three identical samples of the calcined catalyst of Example 6 were treated in 100% steam at 540°C (1,000°F) at atmospheric pressure for either 2, 5, or 10 hours. These steam treated catalysts are designated Catalysts M, N, and O and have the following properties:

Catalyst Designation	Steaming Time, hrs	Phosphorus Content, wt.%	Alpha Activity
M	2	0	10
N	5	0	8
O	10	0	3

A comparison of the alpha activities of the catalysts presented in Example 9 with those presented in Examples 7 and 8 shows that the incorporation of phosphorus into the catalyst composition improves the hydrothermal stability of the catalyst. The catalysts prepared according to Examples 4 and 5 have a higher alpha activity after exposure to steam than the catalyst prepared according to Example 6.

The alpha activity data presented in Examples 4 through 9 are shown graphically in Figure 1.

Example 10

A phosphorus modified fluid catalyst was prepared by first ammonium exchanging as-synthesized (containing the organic directing agent) MCM-22 with 1 N NH_4NO_3, 25 cc/g wet cake. Then a zeolite slurry was prepared by ballmilling the zeolite for 16 hours at 8.8 % solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse N-22) and kaolin clay (Thiele™ RC-32, Thiele Kaolin Co., Sandersonville, GA) was added to the zeolite slurry. Next, phosphoric acid was added to the slurry to result in a phosphorus level of 2.8 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica and then alumina (Condea Pural, SBIII pseudoboehmite alumina) peptized with formic acid. The resulting slurry (18 wt.% solids) was spray dried at an outlet temperature of 177°C (350°F). The spray dried material was calcined for two hours at 540°C (1,000°F) in air. The resulting catalyst is designated Catalyst P and includes about 40 wt.% zeolite. The matrix contains about 50 wt.% clay and about 50 wt.% binder and has a binder silica-alumina ratio of about 5:1.

Example 11

A phosphorus modified fluid catalyst was prepared by first ammonium exchanging as-synthesized (containing the organic directing agent) MCM-22 with 1 N NH_4NO_3, 25 cc/g wet cake. Then the zeolite was nitrogen precalcined for 3 hours at 480°C (900°F). Next, a zeolite slurry was prepared by ballmilling the zeolite for 16 hours at 23 % solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse N-22) and kaolin clay (Kaopaque 10S) was added to the zeolite slurry. Phosphoric acid was added to the slurry to result in a phosphorus level of 3.1 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica and then alumina (Condea Pural, SBIII pseudoboehmite alumina) peptized with formic acid. The resulting slurry (28 wt.% solids) was spray dried at an outlet temperature of 177°C (350°F). The spray dried material was calcined for two hours at 540°C (1,000°F) in air. The resulting catalyst is designated Catalyst Q and includes about 40 wt.% zeolite. The matrix contains about 50 wt.% clay and about 50 wt.% of binder and has a binder silica-alumina ratio of about 5:1.

Example 12

A phosphorus modified fluid catalyst was prepared by first ammonium exchanging as-synthesized (containing the organic directing agent) MCM-22 with 1 N $NH4NO_3$, 25 cc/g wet cake. Then the zeolite was hybrid calcined [e.g., nitrogen precalcined for 3 hours at 480°C (900°F) and then air calcined for 6 hours at 540°C (1,000°F)]. Next, a zeolite slurry was prepared by ballmilling the zeolite for 16 hours at 30 % solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse N-22) and kaolin clay

(Kaopaque 10S) was added to the zeolite slurry. Phosphoric acid was added to the slurry to result in a phosphorus level of 2.9 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica and then alumina (Condea Pural, SBIII pseudoboehmite alumina) peptized with formic acid. The resulting slurry (28 wt.% solids) was spray dried at an outlet temperature of 177°C (350°F). The spray dried material was calcined for two hours at 540°C (1,000°F) in air. The resulting catalyst is designated Catalyst R and includes about 40 wt.% zeolite. The matrix contains about 50 wt.% clay and about 50 wt.% binder and has a binder silica-alumina ratio of about 5:1.

TABLE 5
MCM-22 Preparation

Catalyst Property	P As Synthesized	Q Nitrogen Precalcined	R Hybrid Calcined
Attrition Index, AI	3	12	3
Packed Density, g/cc	0.54	0.64	0.64
Sodium, ppm	1,083	1,215	1,255
Phosphorus, wt.%	2.8	3.1	2.9
Surface Area, m^2/g	193	153	153
Real Density, g/cc	2.3	2.3	2.3
Particle Density, g/cc	0.9	1.0	1.0
Pore Volume, cc/g	0.7	0.6	0.6
Sorption Capacities, g/100 g			
Water	9.2	7.9	7.0
n-Hexane	6.0	4.1	3.0
Cyclohexane	6.0	4.9	4.2
Hydrothermal Stability, Alpha			
Calcined	54	46	8[1]
Steamed @ 540°C, 2 hours	32	27	14
Steamed @ 540°C, 5 hours	25	20	8
Steamed @ 540°C, 10 hours	21	11	6
Steamed @ 790°C, 10 hours (45% H2O, 0 psig)	8	4	3

[1] **Note:**
Upon retesting, this calcined catalyst sample had an alpha activity of 16.

As shown in Table 5, above, the use of hybrid calcined (Catalyst R) or as-synthesized (Catalyst P) MCM-22 resulted in better attrition resistance (lower AI) than the use of nitrogen precalcined MCM-22. Packed density suffered, however, for the as-synthesized catalyst. This catalyst (Catalyst P) also had greater surface area, higher sorption capacities, and a lower particle density than the other two catalysts (Catalysts Q and R). After prolonged steaming time, the nitrogen precalcined (Catalyst Q) or as-synthesized (Catalyst P) catalysts had higher alpha activity than the non-phosphorus containing (Catalysts M, N, and O) and hybrid-calcined (Catalyst R) catalysts.

Example 13

A phosphorus modified fluid catalyst was prepared by first nitrogen precalcining (3 hours at 480°C) as-synthesized (still containing organic directing agent) MCM-22. Next, a zeolite slurry was prepared by ballmilling the zeolite for 16 hours at 25 % solids with deionized water (DI) and using 0.6 wt.% dispersant (Marasperse N-22) and kaolin clay (Kaopaque 10S) was added to the zeolite slurry. Phosphoric acid was added to the slurry to result in a phosphorus level of 1.9 wt.% on the finished catalyst. A silica-alumina binder was then added to the slurry by first adding colloidal silica and then alumina (Condea Pural, SBIII pseudoboehmite alumina) peptized with formic acid. The resulting slurry was immediately spray dried at an outlet temperature of 177°C (350°F). The spray dried material was calcined for two hours at 540° (1,000°F) in air. The calcined material was steam deactivated at 790°C (1,450°F) for 10 hours in 45% steam at atmospheric pressure. The resulting catalyst composition is designated Catalyst S and includes about 25 wt.% zeolite. The matrix contains about 50 wt.% clay and about 50 wt.% binder and has a binder silica-alumina ratio of about 5:1. A control catalyst used in the present study was a rare earth Y type zeolite (REY) catalyst removed from a commercial FCC unit following oxidative regeneration and is designated Catalyst T. Two additional catalysts were prepared for fixed fluidized bed (FFB) testing from Catalyst S and Catalyst T. Catalyst U was prepared from 2 wt.% Catalyst S and 98 wt.% Catalyst T. Catalyst V was prepared from 25 wt.% Catalyst S and 75 wt.% Catalyst T. These cataysts were FFB tested at 515°C (960°F) for 1 minute using a sour heavy gas oil having the properties shown in Table 6. The results of the FFB testing (after interpolation at 70% conversion) are shown in Table 7.

Table 6

Charge Stock Property	Sour Heavy Gas Oil
Pour point, °F (°C)	95 (35)
CCR, wt.%	0.56
Kinematic viscosity, cs @ 40°C	104.8
Kinematic viscosity, cs @ 100°C	7.95
Aniline point, °F (°C)	168.5 (75.8)
Bromine number	6.9
Gravity, API	20.1
Carbon, wt.%	85.1
Hydrogen, wt.%	12.3
Sulfur, wt.%	2.6
Nitrogen, wt.%	0.2
Basic nitrogen, ppm	465
Nickel, ppm	0.5
Vanadium, ppm	0.3
Iron, ppm	1.2
Copper, ppm	<0.1
Sodium, ppm	0.8

TABLE 7

Effect of MCM-22 with Phosphorus on Catalytic Performance
Yield Shifts at 70 vol.% conversion

	Control	Delta Yields	
Catalyst	T	U	V
Zeolite	REY	MCM-22	MCM-22
Percent Additive in Blend	0%	2%	25%
C_5^+ Gasoline, vol.%	52.4	(1.7)	(7.4)
C_4's, vol.%	14.6	0.5	3.8
C_3's, vol.%	10.5	1.6	3.7
C_2^-, wt.%	3.3	(0.2)	-
Coke, wt.%	7.0	(0.1)	1.0
$C_3^=$, vol.%	7.2	0.7	3.1
$C_4^=$, vol.%	5.5	0.2	1.4
$C_5^=$, vol.%	3.7	(0.8)	(0.2)
Potential Alkylate, vol.%	21.0	1.5	7.5
RON, C_5^+ Gasoline	91.5	(1.0)	1.3

( ) denotes a negative value

Claims:

1. A composition comprising a porous crystalline material characterized by an X-ray diffraction pattern including the following lines:

Interplanar d-Spacing (Å)	Relative Intensity, I/I_o x 100
12.36 ± 0.4	M-VS
11.03 ± 0.2	M-S
8.83 ± 0.14	M-VS
6.18 ± 0.12	M-VS
6.00 ± 0.10	W-M
4.06 ± 0.07	W-S
3.91 ± 0.07	M-VS
3.42 ± 0.06	VS

wherein said crystalline material has been treated with a source of phosphorus selected from the group consisting of ammonium monohydrogen phosphate, ammonium dihydrogen phosphate, triammonium phosphate, ammonium hypophosphate, ammonium orthophosphate, ammonium dihydrogen orthophosphate, ammonium monohydrogen orthophosphate, ammonium hypophosphite, ammonium dihydrogen orthophosphite, phosphoric acid and mixtures thereof.

2. A composition as claimed in claim 1 further comprising a matrix material.

3. A composition as claimed in claim 1 or claim 2 further comprising a catalytic cracking component.

4. A composition as claimed in claim 3 wherein the catalytic cracking component is selected from a molecular sieve having a Constraint Index less than 1 and a

mesoporous crystalline material having a pore size of 13 to 200 Angstrom.

5. A composition as claimed in any one of claims 1 to 4 wherein the phosphorous content is greater than 0.1 wt.%.

6. A process of producing a catalyst composition as defined in any one of claims 1 to 5 comprising the step of contacting said zeolite with a source of phosphorus; and forming a catalyst particle from the phosphorus modified zeolite.

7. A process as claimed in claim 6 wherein the phosphorus source is selected from ammonium monohydrogen phosphate, ammonium dihydrogen phosphate, triammonium phosphate, ammonium hypophosphate, ammonium orthophosphate, ammonium dihydrogen orthophosphate, ammonium monohydrogen orthophosphate, ammonium hypophosphite, ammonium dihydrogen orthophosphite, phosphoric acid and mixtures thereof.

8. A process of converting a hydrocarbon feed comprising contacting the feed with a catalyst composition as defined in any one of claims 1 to 5.

9. A catalytic cracking process comprising the step of contacting a heavy hydrocarbon feed with a catalyst composition as defined in claim 3 or 4.

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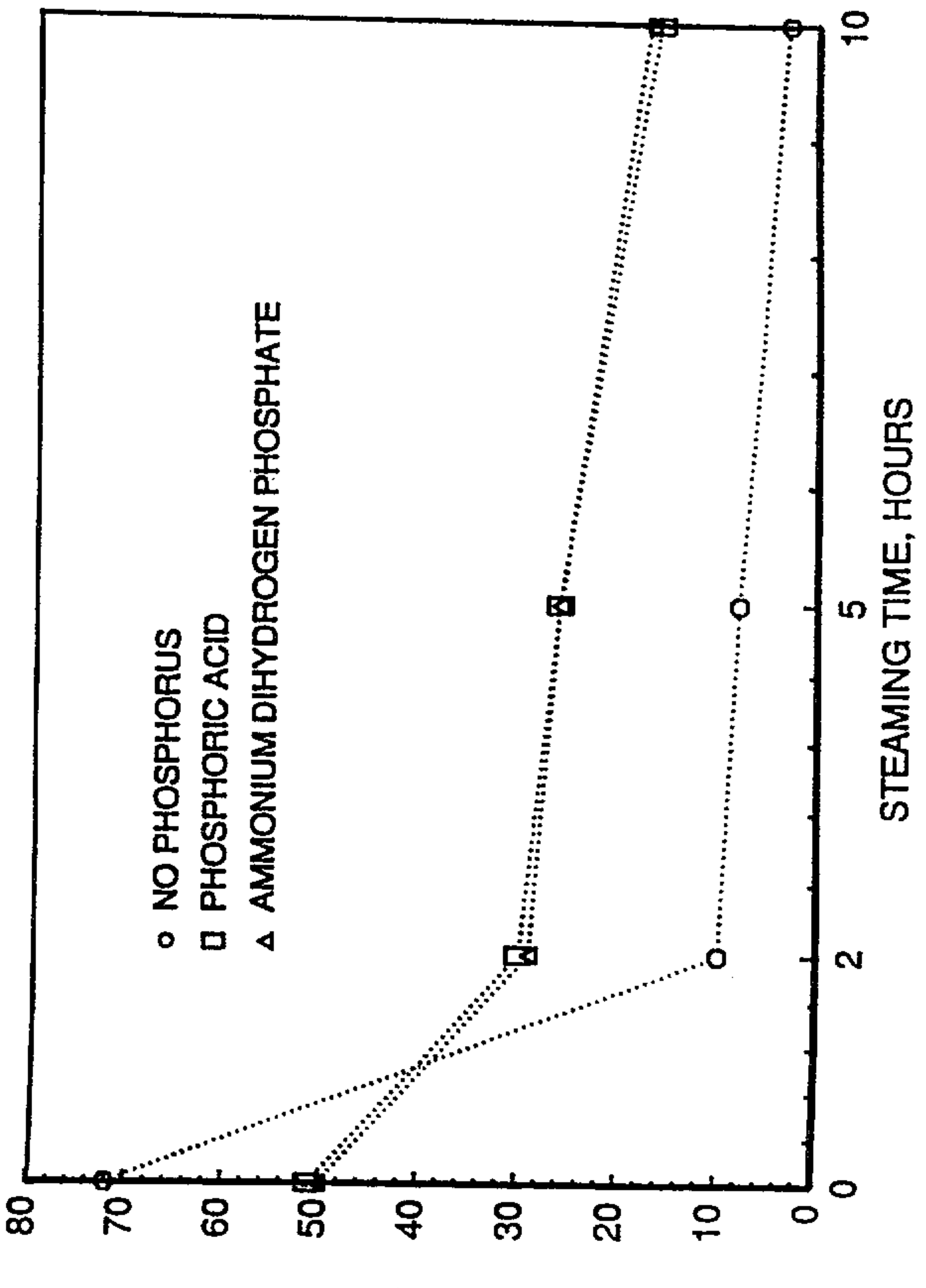
○ NO PHOSPHORUS
□ PHOSPHORIC ACID
△ AMMONIUM DIHYDROGEN PHOSPHATE
ALPHA
80
70
60
50
40
30
20
10
0
0
2
5
10
STEAMING TIME, HOURS