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BECKMANN REARRANGEMENT USING HIERARCHICAL ALUMINOPHOSPHATES AS CATALYSTS

BECKMANN-UMLAGERUNG IN GEGENWART VON HIERARCHISCHEN ALUMOPHOSPHATEN ALS KATALYSATOREN

TRANSPOSITION DE BECKMANN EN PRÉSENCE D'ALUMINOPHOSPHATES HIÉRARCHIQUES EN TANT QUE CATALYSEURS

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Description

FIELD

[0001] The present invention relates to methods of producing lactams, such as ε-caprolactam, for example. In particular, the present invention relates to a method producing ε-caprolactam utilizing aluminophosphate catalysts.

BACKGROUND

[0002] Traditional approaches for producing lactams, used in the production of nylon, include an oxime undergoing a Beckmann rearrangement in the presence of an acid catalyst, such as fuming sulfuric acid.

[0003] Oximes are compounds having the general formula:

\[
\begin{array}{c}
R_1 \\
N \\
R_2 \\
OH
\end{array}
\]

wherein R1 is an organic group and R2 is hydrogen or an organic group. When R2 is hydrogen, the oxime is an oxime derived from an aldehyde, referred to as aldoximes. When R2 is an organic group, the oxime is an oxime derived from a ketone, referred to as ketoximes.

[0004] Cyclic oximes are a sub-group of ketoximes having the general formula:

\[
\begin{array}{c}
R_1 \\
N \\
R_2 \\
OH
\end{array}
\]

wherein the R1 and R2 groups form a ring.

[0005] Lactams, or cyclic amides, are compounds having the general formula:

\[
\begin{array}{c}
R_1 \\
\equiv \\
R_2 \\
N \\
OH
\end{array}
\]

wherein R1 and R2 form a ring.

[0006] Exemplary oximes include, but are not limited, to cyclohexanone oxime, cyclododecanone oxime, 4-hydroxy acetophenone oxime and oximes formed from acetophenone, butraldehyde, cyclopentanone, cycloheptanone, cyclooctanone, and benzaldehyde. Exemplary lactams include those made from cyclic oximes, including those listed above. Lactams are well known in the art as being useful in the production of polyamides, such as nylon. ε-caprolactam can be polymerized to form Nylon-6. ω-laurolactam can be polymerized to form Nylon-12. Additional examples of useful lactams include 11 undecanolactam, a precursor of Nylon-11, 2-Pyrrolidone a precursor of Nylon-4, 2-Piperidone a precursor of Nylon-5.

[0007] Exemplary reactions are shown in FIG. 1. As illustrated in FIG. 1A, cyclohexanone oxime is reacted to form ε-caprolactam. ε-caprolactam in turn is polymerized to form nylon-6. As illustrated in FIG. 1B, cyclododecanone oxime is reacted to form ω-laurolactam. ω-laurolactam in turn is polymerized to form nylon-12. As illustrated in FIG. 1C, cyclooctanone oxime is reacted to form the corresponding lactam (caprylolactam), which in turn can be polymerized to form nylon-8. Nylon-6, nylon-8, and nylon-12 are extensively used in industry and manufacturing.

[0008] One potential reaction mechanism for the reaction of FIG. 1A is illustrated in FIG. 1D. The mechanism generally consists of protonating the hydroxyl group, performing an alkyl migration while expelling the hydroxyl to form a nitrilium ion, followed by hydrolysis, tautomerization, and deprotonation to form the lactam.

[0009] Typically, Beckmann rearrangement reactions of oximes to form lactams are performed using acids such as fuming sulfuric acid. These reactions are characterized by complete or nearly complete conversion of the oxime and very high selectivity for the desired lactams. However, these reactions also produce byproducts including ammonium...
sulfate. Although ammonium sulfate is a useful product in itself, minimizing its production may be desirable.

Different catalysts, such as zeolites have been proposed for use in optimizing the Beckmann rearrangement. It is widely regarded that weak Bronsted sites are required and as such a range of different microporous catalysts, including zeolites, aluminophosphates (AlPO), metal substituted aluminophosphates (MeAlPO), and mesoporous catalysts, including MCM-41 and SBA-15 have been proposed. Zeolites, such as the highly siliceous MFI zeolite catalyst, ZSM-5, have been used in the gas-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

However, typical microporous structures may include one or more disadvantages, including a drop in activity over time due to the formation of carbon deposits on the active sites that act as a poison, reduced mass transfer, diffusion limitations, reduced substrate versatility, and limitations on pore size. Zeotypes having large pores, such as AIPO-8 (AET), VPI-5 (VFI), and cloverite (CLO) may include terminal hydroxyl groups, reducing the stability of the structure. Moreover, these larger pored zeotypes may include strong acid sites, which are less favorable for certain types of reactions, and may not result in increased versatility, longevity, and activity. Mesoporous silicas and isomorphously substituted metals in mesoporous systems, such as Mg-MCM41, Al-MCM41, and MgAl-MCM41, may be less stable, less selective, and less active than microporous catalysts, and their amorphous framework may result in reduced stability.

Improvements in the foregoing processes are desired.

SUMMARY

The present disclosure provides methods for producing lactams from oximes by performing a Beckmann rearrangement using a hierarchical aluminophosphate catalyst. These catalysts are used in reactions to convert oximes into lactams. High conversion of oxime and high selectivity for the desired lactams are produced using the disclosed methods, including improved catalyst longevity, relatively high conversion, and relatively high selectivity for a lactam produced from its corresponding oxime.

Hierarchical porous aluminophosphate catalysts, such as metal-substituted aluminophosphate materials, are provided. Without wishing to be held to any particular theory, it is believed that the hierarchical porous structure provides a microporous structure with desired weak isolated Bronsted acid active sites and a mesoporous network aiding in mass transfer of reactants and products. The network of mesopores is believed to facilitate access to the active sites in the microporous framework of the material. Additionally, in some exemplary embodiments, the hierarchical porous (HP) AlPO materials have large surface areas and pore volumes compared to a corresponding microporous material due to the secondary porosity of the mesoporous network.

A method of performing a Beckmann rearrangement reaction is provided. The method comprises reacting an oxime in the presence of a catalyst to produce a lactam, said catalyst comprising a hierarchical aluminophosphate comprising a microporous framework and a mesoporous framework, wherein the catalyst is a hierarchical porous silicoaluminophosphate catalyst selected from the group consisting of: SAPO-5, SAPO-34, SAPO-37, Co AIPO-5, Ti AIPO-5, and Co Ti AIPO-5, wherein the mesoporous framework has a pore diameter from 20 Å to 50 Å, and wherein the microporous framework has a pore diameter from 3 Å to 10 Å. In a more particular embodiment, the catalyst comprises a plurality of weak Brønsted acid active sites. In a still more particular embodiment, the catalyst does not include any Lewis acid sites.

The catalyst comprises a microporous framework and a mesoporous framework. In one exemplary embodiment, the microporous framework and the mesoporous framework are interconnected.

In one more particular embodiment of any of the above embodiments, the catalyst is a hierarchical porous silicoaluminophosphate catalyst selected from the group consisting of HP SAPO-5, HP SAPO-34, and HP SAPO-37. In a still more particular embodiment, the catalyst is selected from the group consisting of HP SAPO-5 and HP SAPO-34. In one even more particular embodiment, the catalyst is HP SAPO-5. In another even more particular embodiment, the catalyst is HP SAPO-34. In another even more particular embodiment, the catalyst is HP SAPO-37.

In one more particular embodiment of any of the above embodiments, the catalyst is a hierarchical porous aluminophosphate catalyst selected from the group consisting of HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5. In one more particular embodiment of any of the above embodiments, the catalyst is HP Co AIPO-5. In one more particular embodiment of any of the above embodiments, the catalyst is HP Ti AIPO-5. In one more particular embodiment of any of the above embodiments, the catalyst is HP Co Ti AIPO-5.

In one more particular embodiment of any of the above embodiments, the oxime is selected from the group consisting of: cyclohexanone oxime, cyclododecanone oxime, 4-hydroxy aceto phenone oxime and oximes formed from aceto phenone, butyraldehyde, cyclo pentanone, cyclo heptanone, cyclo octanone, and benzaldehyde. In another more particular embodiment of any of the above embodiments, the lactam is selected from the group consisting of: ε-caprolactam, ω-laurolactam, 11-undecanoloactam, 2-Pyrrolidone, and 2-Piperidone. In one more particular embodiment of any of the above embodiments, the oxime is selected from cyclohexanone oxime, cyclo octanone oxime, and cyclododecanone oxime.

In one more particular embodiment of any of the above embodiments, the reaction is performed in the vapor
phase. In another more particular embodiment of any of the above embodiments, the reaction is performed in the liquid phase.

[0021] In a more particular embodiment of any of the above embodiments, the catalyst is phase pure. In another more particular embodiment of any of the above embodiments, the catalyst comprises a plurality of weak Bronsted acid active sites. In still another particular embodiment of any of the above embodiments, the catalyst does not include any Lewis acid sites.

[0022] A method of producing a hierarchical porous aluminophosphate catalyst is provided. The method includes combining a organosilane surfactant, a structure directing agent, and metal precursors to form a mixture, and adding a silicon source to the mixture. The method further includes crystallizing the resulting material to form a catalyst. The method may further comprise crystallizing the catalyst at a temperature of about 200°C for about 24 hours.

[0023] The organosilane surfactant may be dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride. The structure directing agent may be triethylamine and triethylammonium hydroxide. The metal precursor may be aluminum isopropoxide. The silicon source may be silica. The hierarchical porous aluminophosphate catalyst may be a catalyst according to any of the above embodiments.

[0024] The above mentioned and other features of the invention, and the manner of attaining them, will become more apparent and the invention itself will be better understood by reference to the following description of embodiments of the invention taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1A illustrates the reaction from cyclohexanone oxime to ε-caprolactam.
FIG. 1B illustrates the reaction from cyclododecanone oxime to ω-laurolactam.
FIG. 1C illustrates the reaction from cyclooctanone oxime to caprylolactam.
FIG. 1D illustrates the potential steps of a reaction corresponding to a Beckmann rearrangement reaction from cyclohexanone oxime to ε-caprolactam.
FIG. 2 illustrates active sites and pore diameters of an exemplary zeolite, an exemplary mesoporous silica, and exemplary SAPO material, and an exemplary hierarchical SAPO material.
FIG. 3 illustrates Type I, Type II, and Type III isomorphous substitutions in an AlPO material.
FIG. 4A illustrates a pore diameter of an exemplary microporous SAPO-5 material.
FIG. 4B illustrates a pore diameter of an exemplary microporous SAPO-34 material.
FIG. 4C illustrates a pore diameter of an exemplary microporous SAPO-37 material.
FIG. 5 illustrates possible micropore and mesopore active sites in an exemplary hierarchical SAPO material.
FIG. 6 illustrates an exemplary soft-templating technique for forming a hierarchical AlPO material.
FIG. 7A is related to Example 4, and illustrates the X-ray diffraction spectra for SAPO-5 and HP SAPO-5.
FIG. 7B is related to Example 4, and illustrates the X-ray diffraction spectra for SAPO-34 and HP SAPO-34.
FIG. 7C is related to Example 4, and illustrates the X-ray diffraction spectra for SAPO-37 and HP SAPO-37.
FIG. 8A is related to Example 4, and provides the CellRef refinement values for the SAPO-5 material.
FIG. 8B is related to Example 4, and provides the CellRef refinement values for the HP SAPO-5 material.
FIG. 9A is related to Example 4, and provides the CellRef refinement values for the SAPO-34 material.
FIG. 9B is related to Example 4, and provides the CellRef refinement values for the HP SAPO-34 material.
FIG. 10A is related to Example 4, and illustrates the BET adsorption and BJH adsorption pore volume curves for SAPO-5 and HP SAPO-5.
FIG. 10B is related to Example 4, and illustrates the BET adsorption and BJH adsorption pore volume curves for SAPO-34 and HP SAPO-34.
FIG. 10C is related to Example 4, and illustrates the BET adsorption and BJH adsorption pore volume curves for SAPO-37 and HP SAPO-37.
FIG. 11A is related to Example 4 and illustrates an SEM image of SAPO-5.
FIG. 11B is related to Example 4 and illustrates an SEM image of HP SAPO-5.
FIG. 11C is related to Example 4 and illustrates an SEM image of SAPO-34.
FIG. 11D is related to Example 4 and illustrates an SEM image of HP SAPO-34.
FIGS. 12A and 12B are related to Example 4 and illustrate SEM images of HP SAPO-34.
FIG. 13 is related to Example 4 and illustrates an SEM image and EDS data of HP SAPO-34.
FIG. 14 is related to Example 4 and illustrates an SEM image and EDS data of HP SAPO-5.
FIGS. 15 and 16 are related to Example 4 and illustrate a TEM image and elemental analysis of HP SAPO-5.
FIGS. 17-19 are related to Example 4 and illustrate a TEM image and elemental analysis of HP SAPO-34.
FIGS. 20A-20I are related to Example 5 and illustrate the conversion, selectivity, and yield of SAPO-5, HP SAPO-
5, SAPO-34, HP SAPO-34, H-ZSM-5, and MCM-41 for the gas-phase Beckmann rearrangement of cyclohexanone oxime.

FIGS. 21A-21I are related to Example 5 and illustrate the conversion, selectivity, and yield of SAPO-5, HP SAPO-5, SAPO-34, HP SAPO-34, H-ZSM-5, and MCM-41 for the gas-phase Beckmann rearrangement of cyclooctanone oxime.

FIGS. 22A-22C are related to Example 5 and illustrate the conversion and selectivity for the gas-phase Beckmann rearrangement of cyclohexanone oxime with HP SAPO-5 at various temperatures.

FIGS. 23A-23C are related to Example 5 and illustrate the conversion and selectivity for the gas-phase Beckmann rearrangement of cyclohexanone oxime with HP SAPO-34 at various temperatures.

FIGS. 24A-24C are related to Example 5 and illustrate the conversion and selectivity for the gas-phase Beckmann rearrangement of cyclohexanone oxime with HP SAPO-5 at various WHSV.

FIGS. 25A-25C are related to Example 5 and illustrate the conversion and selectivity for the gas-phase Beckmann rearrangement of cyclohexanone oxime with HP SAPO-34 at WHSV.

FIG. 26 is related to Example 6 and illustrates the conversion of cyclododecanone oxime with different catalysts.

FIG. 27A is related to Example 6 and illustrates the conversion of cyclododecanone oxime in the liquid phase with HP SAPO-5 with different quantities of catalyst.

FIG. 27B is related to Example 6 and illustrates the conversion of cyclododecanone oxime in the liquid phase with HP SAPO-34 with different quantities of catalyst.

FIG. 27C is related to Example 6 and illustrates the conversion of cyclododecanone oxime in the liquid phase with HP SAPO-37 with different quantities of catalyst.

FIGS. 28A-28C are related to Example 6 and illustrate the conversion of HP SAPO-34, HP SAPO-5, and HP SAPO-37, respectively, using a liquid recycle set-up.

FIGS. 29A - 29E are related to Example 7 and illustrate NMR spectra for SAPO-5 and HP SAPO-5.

FIGS. 30A - 30E are related to Example 7 and illustrate NMR spectra for SAPO-34 and HP SAPO-34.

FIGS. 31A - 31C are related to Example 7 and illustrate NMR spectra for HP SAPO-37.

FIG. 32A is related to Example 7 and illustrates the FT-IR spectra of SAPO-5 and HP SAPO-5.

FIG. 32B is related to Example 7 and illustrates the FT-IR spectra of SAPO-34 and HP SAPO-34.

FIG. 32C is related to Example 7 and illustrates a comparison of the FT-IR spectra of HP SAPO-5 and HP SAPO-34.

FIG. 33A is related to Example 7 and illustrates the TPD-NP3 results of SAPO-5 and HP SAPO-5.

FIG. 33B is related to Example 7 and illustrates the TPD-NP3 results of SAPO-34 and HP SAPO-34.

FIG. 33C is related to Example 7 and illustrates the TPD-NP3 results of SAPO-37 and HP SAPO-37.

FIG. 34A is related to Example 7 and illustrates the CO adsorption results of HP SAPO-5.

FIG. 34B is related to Example 7 and illustrates the CO adsorption results of HP SAPO-34.

FIG. 35A is related to Example 7 and illustrates the collidine adsorption results of HP SAPO-5.

FIG. 35B is related to Example 7 and illustrates the collidine adsorption results of HP SAPO-34.

FIG. 35C is related to Example 7 and illustrates the collidine adsorption results of HP SAPO-37 and HP Co Ti AIPO-5.

FIG 36A is related to Example 7 and illustrates the 29Si MAS NMR of HP Co AlPO-5.

FIG. 36B is related to Example 7 and illustrates the 29Si MAS NMR of HP Ti AlPO-5.

FIG. 36C is related to Example 7 and illustrates the 29Si MAS NMR of HP Co Ti AlPO-5.

FIG. 37 is related to Example 8 and illustrates the powder X-ray diffraction spectra for HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5.

FIG. 38A is related to Example 8 and illustrates an SEM image of HP Co AlPO-5.

FIG. 38B is related to Example 8 and illustrates an SEM image of HP Ti AlPO-5.

FIG. 38C is related to Example 8 and illustrates an SEM image of HP Co Ti AlPO-5.

FIG. 39A is related to Example 8 and illustrates the nitrogen adsorption isotherm for HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5.

FIG. 39B is related to Example 8 and illustrates the BJH pore distribution curves for HP Co AlPO-5, HP Ti AlPO-5, and HP Co Ti AIPO-5.

FIG. 40A is related to Example 8 and illustrates the 29Si MAS NMR of HP Co AIPO-5.

FIG. 40B is related to Example 8 and illustrates the 29Si MAS NMR of HP Ti AIPO-5.

FIG. 40C is related to Example 8 and illustrates the 29Si MAS NMR of HP Co Ti AIPO-5.

FIG. 41 is related to Example 8 and illustrates the DR UV/vis spectra of the HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5.

FIG. 42 is related to Example 8 and illustrates the FTIR spectra of the OH-stretching region for HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5.

FIG. 43A is related to Example 8 and illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Co AIPO-5.

FIG. 43B is related to Example 8 and illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Ti AIPO-5.

FIG. 43C is related to Example 8 illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Co Ti AIPO-5.

FIG. 44A is related to Example 8 and illustrates the FTIR spectra of 0.02cc of CO adsorbed at 80K on calcined HP
Co AIPO-5, calcined HP Ti AIPO-5 and calcined HP Co Ti AIPO-5.

FIG. 44B is related to Example 8 and illustrates the FTIR spectra of 0.08cc of CO adsorbed at 80K on calcined HP
Co AIPO-5, calcined HP Ti AIPO-5 and calcined HP Co Ti AIPO-5.

FIG. 44C is related to Example 8 and illustrates the FTIR spectra of 0.16cc of CO adsorbed at 80K on calcined HP
Co AIPO-5, calcined HP Ti AIPO-5 and calcined HP Co Ti AIPO-5.

FIG. 45 is related to Example 8 and illustrates the TPD nitrogen adsorption results for HP Co AIPO-5, HP Ti AIPO-
5, and HP Co Ti AIPO-5.

FIG. 46 is related to Example 8 and illustrates a summary of an FTIR collidine probe for HP Co AIPO-5, HP Ti AIPO-
5, and HP Co Ti AIPO-5.

FIG. 47A is related to Example 9 and illustrates the percent conversion, percent selectivity, and percent yield for
the liquid phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam for various catalysts.

FIG. 47B is related to Example 9 and illustrates the percent conversion, percent selectivity, and percent yield for
the liquid phase Beckmann rearrangement of cyclocododecanone oxime to laurolactam for various catalysts.

DETAILED DESCRIPTION

[0026] The present disclosure is directed to a method to form lactams from cyclic oxime compounds. Exemplary
reactions are shown in FIG. 1. As illustrated in FIG. 1A, cyclohexanone oxime is reacted to form ε-caprolactam, which
in turn can be polymerized to form nylon-6. As illustrated in FIG. 1B, cyclododecanone oxime is reacted to form ω-
laurolactam, which in turn can be polymerized to form nylon-12. As illustrated in FIG. 1C, cyclooctanone oxime is reacted
to form caprylolactam, which in turn can be polymerized to form nylon-8. In one exemplary embodiment, a cyclic oxime
having from as little as 5, 6, 8, as great as 10, 12, 18, or greater carbon atoms is reacted to form the corresponding oxime.

[0027] The present method is also useful to perform other Beckmann rearrangement reactions.

[0028] Oximes are converted to lactams, such as in the examples illustrated in FIGS. 1A-1C, through contact with the
catalysts. The present disclosure is believed to be generally applicable to any oxime generated from a variety of aldehydes
and ketones. Exemplary oximes include, but are not limited, to cyclohexanone oxime, cyclododecanone oxime, 4-hydroxy
acetophenone oxime and oximes formed from acetophenone, butyraldehyde, cyclopentanone, cycloheptanone, cy-
clooctanone, benzaldehyde.

[0029] In some exemplary embodiments, the reaction is performed in the absence of a solvent. In some exemplary
embodiments, the reaction is performed in the presence of a solvent. In reactions performed in the absence of a solvent,
the product is used to absorb the exothermic heat produced by the reaction. In these embodiments, a large ratio of
lactam to oxime is maintained in the reaction area to absorb the energy produced by the reaction.

[0030] Exemplary solvents include organic nitriles of the formula:

\[ R^1-CN \]

[0031] Wherein \( R^1 \) represents C1-C8-alkyl, C1-C8-alkenyl, C1-C8-alkynyl, C3-C8-cycloalkyl, C3-C8-aralkyl including a
C9 aromatic ring. Exemplary nitriles include acetonitrile, benzonitrile and mixtures of any of the foregoing.

[0032] Other exemplary solvents include aromatic compounds of the formula:

\[ R^2-Ar \]

[0033] Wherein Ar is an aromatic ring and \( R^2 \) represents H, CH3, F, Cl, or Br. The aromatic ring may be substituted
with one or more \( R^2 \) groups. Exemplary aromatic solvents include benzene, toluene, xylene, and chlorobenzene.

[0034] Still other exemplary solvents include water and alcohols of the formula:

\[ R^3-OH \]

[0035] Wherein \( R^3 \) represents hydrogen, C1-C8-alkyl, C1-C8-alkenyl, C1-C8-alkynyl, C3-C8-cycloalkyl, C3-C8-aralkyl.
Exemplary alcohols include alcohols of 8 or fewer carbon atoms such as methanol, ethanol, n-propanol, iso-propanol,
n-butanol, sec-butanol, iso-butanol, tert-butanol, n-amyl alcohol, n-hexanol, phenol, and mixtures of any of the foregoing.

[0036] In exemplary embodiments, the solvent is rigorously dried prior to contact with the catalyst. As used herein,
rigorously dried is understood to mean dried to a level of 100 ppm water or less. Exemplary methods of drying include
adsorption of water using molecular sieves, such as Activated 4A molecular sieves. As used herein, a reaction performed
in the absence of water means a reaction in which water comprises less than 0.01 wt% of the weight of the reactants.

[0037] The reaction is performed as a liquid phase reaction or a gas phase reaction. As used herein, a liquid phase
reaction in a reaction in which substantially all of the oxime is in the liquid phase when reacted to form the lactam. As
used herein, a gas phase reaction in a reaction in which substantially all of the oxime and solvent is in the gas or vapor

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phase when reacted to form the lactam.

When performed as a gas phase reaction, the reaction is typically performed at a temperature below 350°C. In a more particular embodiment, the reaction is performed at a temperature from about 130°C to about 300°C. In still other embodiments, the reaction may be performed at a temperature as low as about 90°C, 100°C, 110°C, 120°C, 130°C, 135°C, or as high as about 140°C, 150°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, 275°C, 290°C, 300°C, 325°C, 350°C, or within any range defined between any pair of the foregoing values, such as 90°C to 350°C, 100°C to 325°C, or 130°C to 300°C.

When performed as a gas phase reaction, the reaction is typically performed at a pressure from about 0.1 bar to about 1 bar. In some embodiments, a relatively low pressure may be used to provide a high boiling point component in the gas phase without decomposing the component. More particularly, in exemplary embodiments of the reaction performed as a gas phase reaction, the pressure may be as low as about 0.005 bar, 0.01 bar, 0.02 bar, 0.05 bar, 0.1 bar, as high as about 0.5 bar, 1 bar, 10 bar, or higher, or within a range defined between any pair of the foregoing values, such as 0.005 bar to 10 bar, 0.05 bar to 1 bar, or 0.1 bar to 1 bar.

When performed as a liquid phase reaction, the reaction is typically performed at a temperature beneath 250°C. In a more particular embodiment, the reaction is performed at a temperature from about 100°C to about 170°C. In still other embodiments, the reaction may be performed at a temperature as low as about 90°C, 100°C, 110°C, 120°C, 130°C, or as high as about 140°C, 150°C, 170°C, 180°C, 190°C, 200°C, 210°C, 220°C, 230°C, 240°C, 250°C, or within any range defined between any pair of the foregoing values, such as 90°C to 250°C, 100°C to 220°C, or 100°C to 170°C.

When performed as a liquid phase reaction, the reaction is typically performed at a pressure from about 1 bar to about 5 bar. More particularly, in some exemplary embodiments, the pressure may be as low as about 0.5 bar, 1 bar, as high as about 1 bar, 2 bar, 5 bar, 10 bar, 15 bar, 20 bar, 25 bar, 30 bar, 35 bar, or within any range defined between any pair of the foregoing values, such as 0.5 bar to 35 bar, 0.5 bar to 10 bar, or 1 bar to 5 bar. In some exemplary embodiments of the reaction performed as a liquid phase reaction, the solvent is typically a gas at the reaction temperature, but is maintained in the liquid phase by performing the reaction at an elevated pressure.

When performed as a liquid phase reaction, the reaction is typically performed at a temperature and pressure below the critical point of the solvent, where the pressure may be as low as about 1 bar, as high as about 2 bar, 5 bar, 10 bar, 15 bar, 20 bar, 25 bar, 30 bar, 35 bar, or within any range defined between any pair of the foregoing values, such as 1 bar to 35 bar, 1 bar to 10 bar, or 1 bar to 5 bar.

The efficiency of the reaction may be expressed in terms of conversion of oxime, selectivity of the desired product, or yield. Conversion is a measure of the amount of oxime reactant that is consumed by the reaction. Higher conversions are more desirable. The conversion is calculated as:

\[
Conversion(\%) = 100\% \times \left(1 - \frac{\text{moles of oxime remaining}}{\text{moles of oxime supplied}}\right)
\]

Selectivity is a measure of the amount of the desired product that is produced relative to all reaction products. Higher selectivity is more desirable. Lower selectivity indicates a higher percentage of reactant being used to form products other than the desired lactam. The selectivity is calculated as:

\[
Selectivity(\%) = 100\% \times \frac{\text{moles of desired lactam produced}}{\text{moles of oxime supplied} - \text{moles of oxime remaining}}
\]

Yield is a measurement that combines selectivity and conversion. Yield indicates how much of the incoming oxime is reacted to form the desired lactam. The yield is calculated as:

\[
Yield(\%) = \frac{Selectivity(\%) \times Conversion(\%)}{100}\%
\]

The methods according to the present disclosure result in high conversion and selectivity of the desired lactam. In typical embodiments, the conversion is 50% or higher. In a more particular embodiment, the conversion is from about 50% to about 100%. For example, the conversion may be as low as about 50%, 60%, 70%, 75%, or as high as about 80%, 85%, 90%, 95%, 97.5%, 99%, 99.5%, approaching 100%, or 100%, or may be within any range defined between any pair of the foregoing values, such as 50% to 100%, 75% to 99.5%, or 80% to 99%.

In typical embodiments, the selectivity is 50% or higher. In a more particular embodiment, the selectivity is as low as about 50%, 55%, 60%, 65%, or as high as about 70%, 75%, 80%, 85%, 90%, 95%, 97.5%, 99%, 99.5%,
approaching 100%, or may be within any range defined between any pair of the foregoing values, such as 50% to 100%, 75% to 99.5%, or 80% to 99%.

In typical embodiments, the yield is 30% or higher. In a more particular embodiment, the yield is as low as about 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, or as high as about 70%, 75%, 80%, 85%, 90%, 95%, 97.5%, 99%, 99.5%, approaching 100%, or may be within any range defined between any pair of the foregoing values, such as 50% to 100%, 75% to 99.5%, or 80% to 99%.

The methods according to the present disclosure include an oxime reactant undergoing a Beckmann rearrangement reaction in the presence of a catalyst. Referring to Figure 2, exemplary catalysts include natural and synthetic materials, including molecular sieves, microporous materials, such as zeolites 102, aluminophosphate (AlPO) materials (not shown), and silicoaluminophosphate (SAPO) materials 104, and mesoporous materials, such as mesoporous silica 106. As illustrated in Figure 2, the microporous materials, such as zeolite 102 and SAPO 104, illustratively includes one or more micropores 110, and the mesoporous material, such as mesoporous silica 106, illustratively includes one or more mesopores 112. As shown in Figure 2, the micropores 110 and mesopores 112 may include a plurality of active sites 114, such as a hydrogen atom or hydroxyl group.

Aluminophosphates (AlPO) catalysts are microporous materials known to be useful as catalysts. AlPO catalysts include repeating AlO4 and PO4 tetrahedra. It is possible to modify the catalytic properties of a given AlPO catalyst through, for example, the choice of topology, isomorphous substitution, deposition, grafting, and the like. As shown in Figure 3, the aluminum and/or phosphorous atoms in the lattice may be isomorphously substituted. An isomorphous substitution of an aluminum atom with a (+2) or (+3) metal is illustrated as a Type I substitution, an isomorphous substitution of a phosphorous atom with a (+4) metal is illustrated as a Type II substitution, and an isomorphous substitution of both an aluminum and a phosphorous atom with (+4) metal is illustrated as a Type III substitution. Exemplary metals that may be isomorphously substituted to form a Type I substitution include cobalt, copper, nickel, and zinc. Exemplary metals that may be isomorphously substituted to form a Type II substitution include titanium, vanadium, silicon, germanium, and tin.

One exemplary microporous SAPO catalyst, SAPO-5, is illustrated in Figure 4A. SAPO-5 is a silicon-containing aluminophosphate or silicoaluminophosphate catalyst with the International Zeolite Association (IZA) framework code AFI as described in the Atlas of Zeolite Framework Types, 6th ed., Baerlocher, et al., Elsevier, Amsterdam (2007). The SAPO-5 catalyst comprises a plurality of micropores 110 having a pore aperture of 7.3 Å. The catalyst comprises a plurality of silicon atoms 116 isomorphously substituted for phosphorous in the framework, leading to the formation of active sites 114.

One exemplary microporous SAPO catalyst, SAPO-34, is illustrated in Figure 4B. SAPO-34 is a silicon-containing aluminophosphate or silicoaluminophosphate catalyst with the International Zeolite Association (IZA) framework code AFI as described in the Atlas of Zeolite Framework Types, 6th ed., Christian Baerlocher, Lynne B. McCusker and David H. Olson, Elsevier, Amsterdam (2007). The SAPO-37 catalyst comprises sodalite cages linked together through 6,6 (double-6) secondary building units. Twelve of these sodalite cages are then used to create a super-cage structure of which the pore-aperture 110 is 7.4 Å and the internal diameter of the super-cage is in the region of 12-14 Å. The catalyst comprises a plurality of silicon atoms 116 isomorphously substituted for phosphorous in the framework, leading to the formation of active sites 114.

Other exemplary microporous catalysts include AlPO-11 (IZA framework code AEL), AlPO-18 (IZA framework code AEL), AlPO-31 (IZA framework code ATO), AlPO-37 (IZA framework code FAU), AlPO-41 (IZA framework code
The micropores illustrated in Figure 5 are formed by the crystal lattice of the repeating AlO\(_4\) and PO\(_4\) tetrahedra, which may be isomorphously substituted with a silicon atom 116. As illustrated in Figure 5, the SAPO catalyst may include Type II substitutions in the micropores, providing an available proton extending from the lattice into the micropore as a potential Bronsted acid active site 114. As further illustrated in Figure 5, the SAPO may also include Type II substitutions in the much larger mesopores, providing both protons and/or hydroxyl groups extending from the lattice to serve as a potential Bronsted acid active site 114. Without wishing to be held to any particular theory, it is believed that the presence of silanols may provide desirable properties in the catalyst, such as additional hydrophilicity, additional acid sites, the potential to functionalize other active sites, a change in surface area, improved acid site density, and improved acid site strength.

As shown in Figure 5, the micropore framework 110 and mesopore framework 112 are interconnected. Without wishing to be held to any particular theory, it is believed that the micropores 110 possess active sites for catalyzing the Beckmann rearrangement reaction, while the mesopores aid in diffusion of molecules into and out of the active sites. The micropores 110 have the same pore aperture as the microporous SAPO catalyst on which the hierarchical catalyst is based. In contrast, the mesopore 112 in the hierarchical SAPO catalyst 108 illustrated in Figure 5 has a pore diameter larger than pore aperture of the surrounding micropores 110.

In one exemplary embodiment, the hierarchical catalyst includes a plurality of micropores having a total volume as little as 0.05 cm\(^3\)/g, 0.07 cm\(^3\)/g, 0.10 cm\(^3\)/g, 0.12 cm\(^3\)/g, as great as 0.14 cm\(^3\)/g, 0.18 cm\(^3\)/g, 0.20 cm\(^3\)/g, or within any range defined between any two of the foregoing values, such as 0.05 cm\(^3\)/g to 0.10 cm\(^3\)/g or 0.10 cm\(^3\)/g to 0.14 cm\(^3\)/g, and a plurality of mesopores having a total volume as little as 0.05 cm\(^3\)/g to 0.20 cm\(^3\)/g or 0.10 cm\(^3\)/g to 0.14 cm\(^3\)/g, and a plurality of mesopores having a total volume as little as 0.08 cm\(^3\)/g, 0.10 cm\(^3\)/g, 0.11 cm\(^3\)/g, as great as 0.12 cm\(^3\)/g, 0.15 cm\(^3\)/g, 0.17 cm\(^3\)/g, 0.20 cm\(^3\)/g, or within any range defined between any two of the foregoing values, such as 0.08 cm\(^3\)/g to 0.20 cm\(^3\)/g or 0.10 cm\(^3\)/g to 0.15 cm\(^3\)/g. In one exemplary embodiment, the hierarchical catalyst has more surface area and/or pore volume than the corresponding microporous material.
Hierarchical catalysts, such as hierarchical AIPO and SAPO catalysts, may be formed using a soft-templating technique, as illustrated in Figure 6. As illustrated in Figure 6, an organosilane surfactant 120, such as dimethyloctadecyl[(3-(trimethoxysilyl)propyl] ammonium chloride (DMOD), was used in combination with a structure directing agent (SDA) 122 and metal precursors 124. Exemplary structure directing agents 122 include triethylamine and triethylammonium hydroxide. Exemplary metal precursors include aluminum isopropoxide. DMOD is an illustrative surfactant 120 containing an 18 carbon chain and a silicon-containing head. Without wishing to be held to any particular theory, it is believed that the silica portion of the surfactant is incorporated into the SAPO framework, and upon calcination of the organic hydrophobic tail additional silanol sites may be formed. These additional sites may also provide active sites for the Beckmann rearrangement.

Referring to Figure 6, a silicon source, such as silica, is added dropwise, to a mixture of surfactant 120, SDA 122, and metal precursor 124 and stirred. The resulting material is crystalized to form the hierarchical porous SAPO material 108, including both a plurality of micropores 110 from the SAPO crystalline structure, and a plurality of mesopores 112 from the surfactant.

The surfactant may include a carbon chain of as little as 5 carbons, 8 carbons, 10 carbons, 15 carbons, as great as 18 carbons, 20 carbons, 25 carbons, 30 carbons, or greater, or within any range defined between any two of the foregoing values, such as from 5 to 30 carbons, 8 to 25 carbons, or 15-20 carbons. The surfactant may include a silicon-containing head group. The surfactant may include a polar head group containing at least one of carbon, nitrogen, silicon, and phosphorous.

The hierarchical catalyst may be formed from a ratio of aluminum: phosphorous: SDA : water: silica: surfactant of about 1 Al: 1 P: 0.8 SDA: 50 H2O: 0.15 Si: 0.05 surfactant. Exemplary SDAs include triethylamine and triethylammonium hydroxide. Exemplary surfactants include DMOD.

The hierarchical catalyst may be crystallized at a temperature of about 200°C for about 24 hours.

The hierarchical catalyst may be phase pure. The hierarchical catalyst may be a SAPO material that contains amorphous silicon in an amount as little as 1 wt.%, 0.5 wt.%, 0.1 wt.%, 0.05 wt.%, 0.01 wt.%, 0 wt.%, or within any range defined between any two of the foregoing values.

Hierarchical catalysts, such as hierarchical AIPO and SAPO catalysts, may be formed by post synthetic demetallation of a microporous framework. Exemplary reactants for demetallation of a zeolite microporous framework include basic reagents, such as sodium hydroxide, and acidic reagents, such as hydrochloric acid. A microporous catalyst may be added to a base, such as sodium hydroxide, tetrapropylammonium hydroxide with tetrapropylammonium bromide, or to an acid, such as hydrochloric acid. The microporous catalyst may be added to the base or acid in the presence of a surfactant. The microporous catalyst may be added to the base or acid without a surfactant. The material is partially digested, such as at a temperature between 298K and 373K for about 30 minutes. Following treatment, the partially digested material is calcined under air, such as at a temperature of about 550°C for 16 hours, to form the mesoporous material.

Adsorption testing of the hierarchical porous material produces a Type IV isotherm with hysteresis, indicative of polymolecular adsorption of a porous adsorbent.

The hierarchical porous materials may have unit cells consistent with the unit cell of the corresponding microporous materials.

The hierarchical porous materials may have weak, isolated Bronsted acid sites. The hierarchical porous materials may not have Lewis acidity.

The hierarchical porous materials may have isolated, tetrahedral silicon sites. These sites may be similar to isolated, tetrahedral silicon sites of the corresponding microporous material. The hierarchical porous materials may include silanol active sites.

Reference Example 1: Synthesis of a Microporous SAPO-5 (SAPO-5), a Hierarchically Porous SAPO-5 (HP SAPO-5)

The synthetic protocol for the isomorphous substitution of Si into the hierarchically porous AFI framework is described below. An equivalent method was deployed for the synthesis of the microporous analogue without the inclusion of the surfactant dimethyloctadecyl[(3-(trimethoxysilyl)propyl] ammonium chloride (DMOD).

Aluminum isopropoxide (6.807g, Aldrich) was added to a Teflon beaker with phosphoric acid (2.28ml, 85% in H2O, Aldrich) and water (10ml) and vigorously stirred for 1.5 hours until a homogeneous solution was formed. DMOD (1.2ml, 72% in H2O, Aldrich) was added drop wise, followed immediately by addition of triethylamine (3.7ml, Aldrich) drop wise and then water (20ml). The resulting thicker solution was stirred for one hour. Silica sol (0.771ml, 40% in water, Aldrich) was added drop wise and the gel was stirred for a further 1.5 hours to obtain a white gel with the composition: 1 Al: 1 P: 0.8 TEA: 50 H2O: 0.15 Si: 0.05 DMOD.

The gel was divided between three 23 ml Teflon-lined stainless-steel autoclaves which were transferred to a pre heated fan assisted oven (WF-30 Lenton) at 200°C for 24 hours.
The white solid product from each autoclave was collected via filtration and washed with 500ml of deionized water. The product was left to dry at 80°C overnight. The as-synthesized catalyst was calcined in a tube furnace under a flow of air at 550°C for 16 hours to produce a white solid.

Reference Example 2: Synthesis of a Microporous SAPO-34 (SAPO-34) and a Hierarchically Porous SAPO-34 (HP SAPO-34)

The synthetic protocol for the isomorphous substitution of Si into the hierarchically porous CHA framework is described below. An equivalent method was deployed for the synthesis of the microporous analogue without the inclusion of the surfactant dimethyloctadecyl[(3-(trimethoxysilyl)]propyl]ammonium chloride (DMOD).

Aluminium isopropoxide (4.5450g, Aldrich) was added to a Teflon beaker with tetraethylammonium hydroxide (TeaOH) (9.14ml, 35% in H2O, Aldrich) and stirred for one hour. Fumed silica (0.2g) was added slowly and stirred for ten minutes. DMOD (0.8ml, 72% in water, Aldrich) was added drop wise and the white opaque gel stirred for one hour. Deionized water (14ml) was added drop wise followed directly by phosphoric acid (1.5ml, 85% in H2O, Aldrich). The gel was stirred vigorously for two hours to produce a white gel with the composition: 1 Al: 1 P: 1 TeaOH: 65 H2O: 0.15 Si: 0.05 DMOD.

The contents of the gel were divided between two 23 ml Teflon-lined stainless-steel autoclaves which were transferred to a pre heated fan assisted oven (WF-30 Lenton) at 200°C for 24 hours.

The white solid product from each autoclave was collected via filtration and washed with 500ml of deionized water. The product was left to dry at 80°C overnight. The as-synthesized catalyst was calcined in a tube furnace under a flow of air at 550°C for 16 hours to produce a white solid.

Reference Example 3: Synthesis of a Microporous SAPO-37 (SAPO-34) and a Hierarchically Porous SAPO-37 (HP SAPO-37)

The synthetic protocol for the isomorphous substitution of Si into the hierarchically porous FAU framework is described below. An equivalent method was deployed for the synthesis of the microporous analogue without the inclusion of the surfactant dimethyloctadecyl[(3-(trimethoxysilyl)]propyl]ammonium chloride (DMOD).

Boehmite (5.5844g) was added slowly to a solution of phosphoric acid (85wt.%, 9.251g) and deionized water (10g) in a Teflon beaker. The thick white mixture was stirred magnetically for 7 hours and labelled solution A.

Solution B was prepared by adding DMOD (72wt.%, 2ml) drop wise to a solution of tetra propyl ammonium hydroxide, TPAOH (40wt.%, 38.689g) and tetra methyl ammonium hydroxide. TMAOH (0.365g), followed by fumed silica (1g). Solution B was stirred for 2 hours.

Once both solution A and B were homogenized solution B was added drop wise to solution A to create a very thick mixture. This was stirred for 68 hours. Then transferred to autoclaves and crystallized at 200°C for 24 hours.

The resulting white solid was filtered with 1 liter of deionized water and left to dry in an oven (80°C) overnight. The catalyst was then calcined at 550°C for 16 hours under air to yield a white solid.

Reference Example 4: Characterization of Catalysts

Powder X-ray Diffraction

Powder X-Ray diffraction (pXRD) patterns were obtained using a Bruker D2 diffractometer using Cu Kα1 radiation where $\lambda = 1.54056$. Low angle X-ray diffraction patterns were obtained using a Bruker C2 GADDS diffractometer. The hierarchical catalysts were confirmed to retain their parent unit cells via pXRD (Figures 7A-7C). The corresponding lattice parents were similar to the microporous analogues (see, e.g. Figures 8A, 8B, 9A and 9B) and confirmed that the hierarchical catalysts were phase pure and retained their crystallinity.

As shown in Figure 7A-7C, the phase purity and crystallinity of all materials were confirmed via powder X-ray diffraction. All signals can be attributed to the corresponding AFI, CHA, or FAU structure according to the IZA database. The CellRef refinement values for the calcined AFI and CHA catalysts are presented as Figures 8 and 9. The results were consistent with the expected AFI framework for SAPO-5 and HP SAPO-5, and the expected CHA framework for SAPO-34 and HP SAPO-34.

Low angle XRD measurements of the hierarchical samples, shown in the inserts of Figures 7A and 7B, revealed a peak at low angles, which was absent in the microporous samples. This peak indicates the presence of mesopores in the hierarchical samples.
Nitrogen adsorption desorption experiments were performed using a Gemini 2575 Brunauer-Emmett-Teller (BET) Apparatus with nitrogen as the adsorption gas at 77K. BET measurements for each catalyst are presented in Table 1. As shown in Table 1, the hierarchical catalysts had higher overall surface area ($S_{BET}$), higher micropore volume ($V_{micro}$), and higher mesopores volume ($V_{meso}$) than the corresponding microporous materials.

The N$_2$ adsorption desorption isotherms of HP SAPO-5, HP SAPO-34, and SAPO-37, shown in Figures 10A-10C, are typical of a type IV isotherm with a hysteresis. The exhibited type IV isotherms with hysteresis for the hierarchical porous materials are consistent with the presence of mesopores in the corresponding hierarchical frameworks.

The BJH adsorption pore volume curves provided as inserts in Figures 10A-10C further confirm the presence of mesopores having a diameter between about 20Å and about 60Å in the hierarchical systems, as well as the absence of such mesopores in the microporous materials.

The hierarchical catalysts exhibited type IV isotherms (Figures 10A-10C) with hysteresis, which is consistent with the presence of mesopores. The surface areas and mesopore volumes were also higher in the hierarchical catalysts compared to the microporous analogues, consistent with incorporation of mesopores into the hierarchical frameworks (Table 1). The BJH adsorption pore distribution curves further support the presence of mesopores in the hierarchical systems and the absence of such mesopores in the microporous catalysts (Figures 10A-10C).

The hierarchical materials porosity was further evaluated via scanning electron microscopy (SEM) (Figures 11-14). Figure 11A illustrates the elongated hexagonal crystals of microporous SAPO-5. Figure 11B illustrates the crystals of the hierarchical porous HP SAPO-5. Figure 11C illustrates cubic crystals of microporous SAPO-34. Figure 11D illustrates the crystals of the hierarchical porous HP SAPO-34. The hierarchical porous material images in Figures 11B and 11D depict larger particles than the corresponding microporous materials in Figures 11A and 11C. The hierarchical materials appear to include aggregates of smaller crystals.

As shown in Figures 12A and 12B, the HP SAPO-34 is composed of blocky, well-dispersed crystals, as well as larger agglomerations of possible intergrown and less-dispersed crystals.

The SEM images indicated the samples have a fairly uniform composition throughout the sample. As shown in the SEM image and corresponding energy dispersive (EDS) data of Figure 13, the composition of the HP SAPO-34 is fairly uniform. As shown in the SEM image and corresponding energy dispersive (EDS) data of Figure 14, the composition of the HP SAPO-5 is fairly uniform.

The hierarchical materials porosity was further evaluated via transmission electron microscopy (TEM) (Figures 15-19). The TEM images indicated the samples having a fairly uniform composition throughout the sample, and revealed fine mesoporosity in both the crystalline HP SAPOs (see Figures 17-19).

As shown in the TEM image an elemental analysis of Figure 15, the HP SAPO-5 material had regions of mesoporosity in the faulted region 130. The elemental analysis of the ratio of Al:Si:P, was as expected for a SAPO material.

The lattice crystal structure of each of the HP SAPO-5 and HP SAPO-34 was confirmed. As shown in Figure 16, the diffraction pattern of the selected portion of the HP SAPO-5 material was confirmed to be AFI. The elemental analysis in Figure 15 is consistent with the expected Al:P:Si ratio for a SAPO material.

From the TEM and diffraction patterns of HP SAPO-34 it was possible to elucidate the rod like and elongated shapes of the mesopores and their positioning perpendicular and parallel to the rhombohedral basis vectors. It was clear that these mesopores were well connected within the microporous network. (Figures 17, 18). As shown in Figure 17,
the diffraction pattern of the selected portion of the HP SAPO-5 material was confirmed to be AFI. The elemental analysis in Figure 17 is consistent with the expected Al:P:Si ratio for a SAPO material. The two reflections (101) (RHS ref1) and (-1,1,1) (RHS ref 2) are equivalent to (100) and (101), the pores therefore appear to have rod-like morphology, elongated parallel to one or another to the rhombohedral basis vectors. As shown in Figure 18, which includes a TEM image and diffraction pattern of HP SAPO-34 from the same location, the indexing indicates that the pores are elongated perpendicular to the (101) plane. This is equivalent to the (100) of the rhombohedral type unit cell.

**[0105]** The TEM image and EDS of the HP SAPO-34 in Figure 19 further show the presence of some secondary porosity 132.

**Example 5: Vapor Beckmann Rearrangement of Cyclohexanone Oxime and Cyclooctanone Oxime**

**[0106]** The catalytic performance of the hierarchical HP SAPO-5 and HP SAPO-34 samples was compared to that of the microporous SAPO-5 and SAPO-34 samples. A vapor Beckmann rearrangement of cyclohexanone oxime (see Figure 1A) was performed for each pair of hierarchical and microporous catalysts.

**[0107]** A cylindrical quartz fixed bed reactor (4mm in diameter) with a quartz frit was packed with 0.5 cm layer of glass beads (1mm), a 4 cm layer of pelletized catalyst (0.2g), and a further 20cm of glass beads (1mm) were placed inside the heater unit of the reactor assembly. The sample was then pre-treated at 673K under a 50ml/min flow of helium gas for one hour. The temperature was then lowered to 598K and the flow of helium was reduced to 33.3ml/hour. A liquid feed of 100 g/litre of cyclohexanone oxime in ethanol was fed into the reactor to maintain a WHSV of 0.79hr⁻¹ that was controlled by an electronic syringe pump. A sample was taken after every hour when steady state was achieved. Samples were analyzed using a PerkinElmer Clarus 480 gas chromatogram with FID and using an Elite 5 column, the peak areas were calibrated using pre-determined response factors with mesitylene as an internal standard.

**[0108]** The feed solution for assessing the carbon balance using mesitylene as the internal standard was composed of: Mesitylene: 0.444g; Cyclohexanone oxime: 4.10g; EtOH: 36.000g

**[0109]** Performing an identical procedure to one described above the following GC data was obtained at 598K, WHSV of 0.79hr⁻¹ with HP SAPO-5 and by using the response factors it was possible to calculate the number of moles from the peak areas.

**[0110]** Figure 20A shows the conversion of the microporous SAPO-5 and of the hierarchical HP SAPO-5, and Figure 20B shows the selectivity for ε-caprolactam of the reaction. Figure 20C shows the corresponding yield for the reactions. **[0111]** Figure 20D shows the conversion of the microporous SAPO-34 and of the hierarchical HP SAPO-34, and Figure 20E shows the selectivity for ε-caprolactam of the reaction. Figure 20F shows the corresponding yield for the reactions. **[0112]** As shown in Figures 20A-20F, the hierarchical catalysts provided superior performance compared to the microporous catalysts. The hierarchical catalysts were able to maintain both a constant conversion (Figures 20A, 20D), and relatively constant selectivity (Figures 20B, 20E), while the corresponding microporous catalysts appeared to deactivate. For example the HP SAPO-5 retains a >97% conversion whereas SAPO-5’s activity started at 71% and dramatically dropped to just 33% over 7 hours.

**[0113]** The performance of the industrial microporous catalyst H-ZSM-5 and the mesoporous MCM-41 catalysts was also investigated. The conversion of H-ZSM-5 and MCM-41 is shown in Figure 20G, and the selectivities for ε-caprolactam are shown in Figure 20H. Figure 20I shows the corresponding yield for the reactions.

**[0114]** The microporous H-ZSM-5 catalyst, similar to the microporous SAPO-5 and SAPO-34, appeared to quickly deactivate. The mesoporous catalyst MCM-41 was quickly deactivated and exhibited much lower initial conversion and selectivity than the hierarchical catalysts.

**[0115]** The hierarchical materials generally provided high conversion and selectivity, as well as generally improved longevity compared to the remaining materials. Without wishing to be bound by any particular theory, it is believed that the microporous framework of the hierarchical catalysts provided active sites for the Beckmann rearrangement reaction, and that the connected mesopores provided enhanced diffusion of the cyclic oximes and/or lactams to and from the active sites.

**[0116]** An identical protocol was followed for the vapor phase Beckmann rearrangement of the more sterically demanding cyclooctanone oxime to form the corresponding caprylolactam (see Figure 1C).

**[0117]** Figure 21A shows the conversion of the microporous SAPO-5 and of the hierarchical HP SAPO-5, and Figure 21B shows the selectivity for the desired lactam. Figure 21C shows the corresponding yield for the reactions. **[0118]** Figure 21D shows the conversion of the microporous SAPO-34 and of the hierarchical HP SAPO-34, and Figure 21E shows the selectivity for the desired lactam. Figure 21F shows the corresponding yield for the reactions. **[0119]** Figure 21G shows the selectivity of the microporous H-ZSM-5 and the mesoporous MCM-41, and Figure 21H shows the selectivity for the desired lactam. Figure 21I shows the corresponding yield for the reactions. **[0120]** For the cyclooctanone oxime reaction, both hierarchical catalysts provided relatively good selectivity. **[0121]** With respect to SAPO-5 and HP SAPO-5, the selectivity was seen to increase over time. Without wishing to be held to any particular theory, this may suggest that that some of the original strong acid sites become blocked during
As shown in Figure 23A, a similar experiment was conducted using HP SAPO-34 as the catalyst. The reaction of the reaction for solution of the oxime in ethanol. The reaction was run at 300°C, 325°C, 350°C, and 400°C. The conversion and selectivity function of time is shown in Figures 23B and 23C.

As with the cyclohexanone oxime reaction, the hierarchical catalysts retained their high activities with cyclooctanone oxime over 7 hours, whereas the activities of the microporous catalysts were reduced significantly. In particular, the HP SAPO-34 is just as active in the rearrangement of cyclohexanone oxime as the rearrangement of cyclooctanone oxime, but the activity of the comparative microporous SAPO-34 in the rearrangement of cyclooctanone oxime is much lower, similar to H-ZSM-5.

As shown in Figure 23A, a similar experiment was conducted using HP SAPO-34 as the catalyst. The reaction was run at 0.8 hr\(^{-1}\) and 1.6 hr\(^{-1}\) cyclohexanone oxime. The conversion and selectivity of the reaction for ε-caprolactam as a function of time is shown in Figures 22B and 22C.

As shown in Figures 20 and 21, the hierarchical catalysts provided similar active sites compared to their microporous analogues, while retaining high conversion levels over the course of the observed reaction time.

The effect on the reaction of temperature was investigated. As shown in Figure 22A, a weight hourly space velocity (WHSV) of 0.79 hr\(^{-1}\) cyclohexanone oxime were provided to a reactor containing 0.2 g of catalyst as a 10 wt.% solution of the oxime in ethanol. The reaction was run at 300°C, 325°C, 350°C, and 400°C. The conversion and selectivity of the reaction for ε-caprolactam as a function of time is shown in Figures 22B and 22C.

As shown in Figures 22A-22C and 23A-23C, both HP SAPO-5 and HP SAPO-34 are stable in the vapor phase Beckmann rearrangement of cyclohexanone oxime over a range of temperatures. High selectivities and conversions are retained over the reaction time and structural integrity of the catalyst was also maintained.

The effect on the reaction of oxime concentration was investigated. As shown in Figure 24A, cyclohexanone oxime was provided to a reactor containing 0.2 g of catalyst as a 10 wt.% solution of the oxime in ethanol. The reaction was run at 325°C

The flow rate of cyclohexanone oxime was varied between 0.8 hr\(^{-1}\) and 1.6 hr\(^{-1}\). The conversion and selectivity of the reaction for ε-caprolactam as a function of time is shown in Figures 24B and 24C.

As shown in Figure 23A, a similar experiment was conducted using HP SAPO-34 as the catalyst. The reaction was run at 0.8 hr\(^{-1}\), and 1.6 hr\(^{-1}\) cyclohexanone oxime. The conversion and selectivity of the reaction for ε-caprolactam as a function of time is shown in Figures 25B and 25C.

As shown in Figures 24 and 25, HP SAPO-5 and HP SAPO-34 maintain high conversion and selectivity over a range of WHSV values, further supporting the stability and versatility of the catalysts.

Example 6: Liquid Beckmann Rearrangement of Cyclohexanone Oxime and Cyclooctanone Oxime

Cyclohexanone oxime (0.1g), internal standard anhydrous chlorobenzene (0.1g) and freshly calcined catalyst (0.1g) were added to anhydrous benzonitrile (20ml) in a 3-necked batch reactor flask at 130 °C under reflux and nitrogen. The resulting suspension was stirred magnetically at the reaction temperature. Over the course of the reaction aliquots of the reaction mixture were taken and analyzed via GC.

The conversions of the HP SAPO-5, HP SAPO-34 and HP SAPO-37 catalysts in the liquid phase rearrangement of cyclododecanone oxime to laurolactam as a function of time are provided in Figure 26. The reaction was run at 130°C under nitrogen with PhCN (20ml) as the solvent. 0.1g of the catalyst was provided to the reactor along with 0.1g of the oxime, and allowed to reflux for 7 hours.

As shown in Figure 26, comparative performance of the microporous and hierarchical catalysts in the liquid-phase Beckmann rearrangement of cyclododecanone oxime, with the hierarchical analogues displaying enhanced rates at lower contact times. In addition, the smaller pore (3.8Å) microporous SAPO-34 has a much inferior performance (mass-transfer and diffusion limitations) compared with its hierarchical analogue, thereby highlighting the catalytic potential of the latter with bulkier substrate molecules. HP SAPO-5, HP SAPO-34 and HP SAPO-37 are all active in the liquid phase Beckmann rearrangement of cyclododecanone oxime to laurolactam. They each reach 100% conversion with 100% selectivity by 5 hours. All the HP SAPOs are more active than their microporous analogues, illustrating the benefits of having more accessible active sites within a hierarchically porous framework.

The effect on the reaction of cyclododecanone oxime of the amount of catalyst was investigated. As shown in
Figures 27A-27C, the amount of catalyst was varied from 0.02g catalyst per 0.1g oxime to 0.1g catalyst per 0.1g oxime. Figure 27A illustrates the results for HP SAPO-5. Figure 27B illustrates the results for HP SAPO-34. Figure 27C illustrates the results for HP SAPO-37.

[0136] The effect on the reaction of cyclododecanone oxime catalyzed with HP SAPO-34 of the temperature was investigated. The results are provided in Table 2.

Table 2: Conversion, selectivity, and yield of cyclododecanone oxime at various temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Time (minutes)</th>
<th>Conversion (mol%)</th>
<th>Selectivity (mol%)</th>
<th>Yield (mol%)</th>
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</thead>
<tbody>
<tr>
<td>110</td>
<td>60</td>
<td>26.3</td>
<td>100</td>
<td>26.3</td>
</tr>
<tr>
<td>110</td>
<td>120</td>
<td>44.2</td>
<td>100</td>
<td>44.2</td>
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</tbody>
</table>

[0137] As shown in Table 2, HP SAPO-34 has been tested over a range of reaction temperatures including 110°C, 130°C and 150°C. The rate of reaction improved significantly as a function of increasing temperature. Under all the conditions the catalyst reaches maximum conversion with 100% selectivity to the desired lactam.

[0138] Referring next to Figures 28A-28C, a recycle experiment was conducted for each catalyst for the Beckmann rearrangement of cyclododecanone oxime. Cyclohexanone oxime, internal standard anhydrous chlorobenzene, and freshly calcined recovered catalyst were added to anhydrous benzonitrile in a 3-necked batch reactor, with a 1:1:1:30.6 weight ratio respectively, at 130°C under reflux and nitrogen. The resulting suspension was stirred magnetically at the reaction temperature. Over the course of the reaction aliquots of the reaction mixture were taken and analyzed via GC. Conversion was determined after 7 hours. Figure 28A illustrates the change in percent conversion for each recycle using the HP SAPO-34 catalyst. Figure 28B illustrates the change in percent conversion for each recycle using the HP SAPO-5 catalyst. Figure 28C illustrates the change in percent conversion for each recycle using the HP SAPO-34 catalyst.

[0139] As illustrated in Figures 28A-28C, HP SAPO-5, HP SAPO-34 and HP SAPO-37 all retain structural integrity and demonstrated sustained catalytic performance (near 100% conversion) after the recycle tests.

Reference Example 7: Characterization of Catalysts Acidic Properties

[0140] From Example 4, it was observed that the hierarchical catalysts exhibited improved longevity in the reactions.
This suggests minimal coking is occurring in these systems. Coking can occur if acid sites are too strong and therefore, do not permit the desorption of the product, or it can occur if diffusion is hindered therefore preventing the egress of products. Without wishing to be bound by any particular theory, it is believed that the hierarchical catalysts acidity is attenuated by the presence of mesopores and that the mesopores are aiding the mass transport of substrates and products.

Therefore to further establish the origin of these improvements, the structural properties (N₂ adsorption desorption isotherms and electron microscopy) and acidic properties (NMR, TPD-NH₃ FT-IR using CO and collidine as a probe molecule) of the catalysts were further investigated.

Solid state NMR

Figure 29A illustrates the ²⁷Al MAS NMR spectra of SAPO-5. Figure 29B illustrates the ²⁷Al MAS NMR spectra of HP SAPO-5. Figure 30A illustrates the ²⁷Al MAS NMR spectra of SAPO-34. Figure 30B illustrates the ²⁷Al MAS NMR spectra of HP SAPO-34.

Figure 29C illustrates the ³¹P MAS NMR spectra of SAPO-5. Figure 29D illustrates the ³¹P MAS NMR spectra of HP SAPO-5. Figure 30C illustrates the ³¹P MAS NMR spectra of SAPO-34. Figure 30D illustrates the ³¹P MAS NMR spectra of HP SAPO-34.

The ²⁷Al and ³¹P MAS NMR support the formation of a fully condensed crystalline AlPO framework. The ²⁷Al MAS/NMR has a strong signal at around -35 to -37 ppm indicating the presence of tetrahedral aluminium. Although there are weaker signals at around -16 and 8ppm indicating the presence of hydrated aluminium centres which are octahedral and five coordinate respectively.

Figure 29E illustrates the ²⁹Si MAS NMR spectra of SAPO-5 and HP SAPO-5. The spectra may suggest that the presence of the surfactant encourages the formation of silicon islands and results in silica nests, which are absent in the microporous system.

Figure 30E illustrates the ²⁹Si MAS NMR spectra of SAPO-34 and HP SAPO-34. The Si NMR supports the formation of isolated silicon sites which are comparable to the microporous analogue.

FT-IR, NH₃, CO and Collidine probes

To further investigate the acidic properties of the resulting hierarchical catalysts FT-IR with probe molecules (CO and collidine) was used. FT-IR permitted direct observation of the hydroxyl region of the hierarchical SAPOs.

The FT-IR spectra of SAPO-5 and HP SAPO-5 are presented in Figure 32A, and the FT-IR spectra of SAPO-34 and HP SAPO-34 are presented in Figure 32B. Both catalysts had bands attributable to POH/AlOH (3678cm⁻¹) defect sites and bands (3628-3600cm⁻¹) arising from the substitution of silicon into the framework (Si-OH-Al). There was also an additional band at 3746cm⁻¹ that were assigned to defect Si-OH groups which were marginal in the FT-IR of the microporous catalysts indicating that these silanol sites were formed via the calcination of the surfactant.

A comparison of the FT-IR spectra for HP SAPO-5 and HP SAPO-34 is presented in Figure 32C. As shown in Figure 32C, the hierarchical porous materials share a common Si-OH peak (~3750cm⁻¹) that is significantly greater than in the spectra of the corresponding microporous SAPO-5 and SAPO-34 (see Figures 32A and 32B).

The quantity and strength of acid sites was investigated using a programmed temperature desorption of ammonia (TPD) for SAPO-5 and HP SAPO-5, the results of which are presented in Figure 33A, for SAPO-34 and HP SAPO-34, the results of which are presented in Figure 33B, and for SAPO-37 and HP SAPO-37, the results of which are presented in Figure 33C.

All TPD measurements were performed on a custom built system using TCD detectors to monitor ammonia concentration. Samples were pre-treated by heating at 10°C/min to 550°C in a 20% O₂/Helium mixture for 2 hours. The samples were exposed to ammonia and allowed to equilibrate at 150°C for 8 hours. Desorption was performed in flowing at 10°C /min to 600°C and held for 40 minutes at 600°C.

The results indicated similar acid strength between SAPO-5 and HP SAPO-5 (see Figure 33A), between SAPO-34 and HP SAPO-34 (see Figure 33B), and between SAPO-37 and HP SAPO-37 (see Figure 33C). Without wishing to be held to any particular theory, it is believed that the slight additional feature in Figure 33B at 250-300°C may be attributable to the weakly acidic silanol sites and further allude to the presence of the SiOH sites in the hierarchical catalysts.

While the FT-IR spectra provided information about the types of hydroxyl groups present, it did not discriminate regarding the strength and type of acid sites present in the hierarchically porous materials. The acid strength of these materials is believed to be related to the ensuing catalytic properties of the materials. Without wishing to be held to any particular theory, the Beckmann rearrangement with solid acid catalysts is believed to rely on a subtle balance of acidity.
within the active site; it needs to be strong enough to permit the reaction to perform but weak enough to enable the basic lactam to desorb before over reacting, coke formation and deactivation.

Characterization of the strength of the acid sites was investigated using probe molecules such as CO and 2,4,6-trimethylpyridine (collidine) with the FT-IR to indirectly study the acidity of the material. The absence of absorption ≥ 2190 cm⁻¹ in Figures 34A and 34B indicates that no Lewis acidity was observed in either the HP SAPO-5 or the HP SAPO-34 materials, and that only Bronsted acid sites were present. Evaluation of the band shift of the Bronsted acid sites between 260 and 286 cm⁻¹ upon interaction with CO revealed that both samples primarily consisted of moderate strength Bronsted acid sites. By integrating the area of the Bronsted acid peaks it was possible to ascertain that the HP SAPO-34 has more total Bronsted acidity, as well as some stronger acid sites (larger peak shift) compared the HP SAPO-5 sample. These results were similar to the ammnia temperature programmed desorption results shown in Figures 33A and B, and the FT-IR collidine data shown in Figures 35A and 35B. The strength of acidity of the hierarchical catalysts was similar to the acid strength of microporous catalysts, indicating that the hierarchical porous material has similar active sites to those of the corresponding microporous materials.

FT-IR with CO demonstrated that in both HP SAPO-5 (see Figure 34A) and HP SAPO-34 (see Figure 34B) no Lewis acidity was observed, characterized by an absence of absorption ≥ 2190 cm⁻¹. Instead only Bronsted acid sites were present. Evaluation of the band shift of the Bronsted acid sites between 260-286 cm⁻¹ upon interaction with CO (Table 2) revealed that both samples primarily consisted of moderate strength Bronsted acid sites. Table 3 provides the position of maxima of OH Bronsted sites and their shifts (ΔvOH) upon CO Adsorption at 80K on HP SAPO-34, HP SAPO-5 and their microporous analogues.

By integrating the area of the Bronsted acid peaks it was possible to ascertain that the HP SAPO-34 has more total Bronsted acidity, as well as some stronger acid sites (larger peak shift) compared the HP SAPO-5 sample. This trend was in good agreement with the ammnia temperature programme desorption results (Figures 33A and 33B). The results in Table 3 further indicated that the hierarchical catalysts have active sites that are similar to those in the corresponding microporous catalysts.

In order to further explore the acid sites within the hierarchical SAPOs, collidine was used as a probe with FT-IR. Collidine was chosen for three key reasons: i) It is a sterically demanding probe and therefore provides insight into the accessibility of the acidic sites, ii) It can assess the strength of interaction between the OH...N, by quantifying the bands at 1652 cm⁻¹ and 1637 cm⁻¹, hence allude to the strength of interaction between the substrates in the Beckmann rearrangement and finally iii) It is stable at high temperatures and therefore the strength of interaction can be screened over temperatures typical of the reaction conditions.

Figure 35A illustrates the results of the collidine adsorption on HP SAPO-5. The collidine interacts with all of the OH group types after 150°C desorption. Essentially all the collidine is desorbed by 450°C. Figure 35B illustrates the distribution of weak, medium, and strong acid sites in the SAPO-5 and HP SAPO-5 catalysts. As shown in Figure 35B, the HP SAPO-5 catalyst generally contains a greater number of weak, medium, and total acid sites than the SAPO-5 catalyst. In the case of the HP SAPO-5 the collidine is able to interact with all the OH group types (Si-OH, P-OH, Si-OH-Al and the H-bonded) after 150°C desorption and their accessibility is greatly enhanced in comparison to the microporous analog SAPO-5.

Figure 36A illustrates the results of the collidine adsorption on HP SAPO-34. The collidine interacts primarily with all of the OH group types after 150°C desorption. Essentially all the collidine is desorbed by 450°C. Figure 36B illustrates the distribution of weak, medium, and strong acid sites in the SAPO-34 and HP SAPO-34 catalysts. As shown in Figure 36B, the HP SAPO-34 catalyst has a similar distribution of acid sites compared to the SAPO-5 catalyst. As shown in Figure 36A, similar to the microporous structure only a small fraction of the bridging OH groups are accessible to collidine as there is very minimal attenuation of the bridging hydroxy groups.

The differences between the accessibility of the two hierarchical catalysts active sites could be explained by their very different microporous structures (see Figures 4A and 4B). SAPO-5 has much larger pores, 7.3 Å, than SAPO-
34, 3.8Å. As the hierarchical materials are largely microporous, it is likely that not all the mesopores are accessible owing to them being surrounded by the microporous system, and therefore the FT-IR-collidine may not truly represent all the types of acid sites that are present. In both cases all the collidine is desorbed by 450°C. Similar to the FT-IR-CO results, the collidine adsorption indicates that the collidine largely adsorbs onto moderate to weak acid sites.

[0162] The hierarchical catalysts, such as HP SAPO-5 and HP SAPO-34, had comparable acidity to their corresponding microporous analogues, but provided improvements in one or more of lifetime, activity and substrate versatility in the Beckmann rearrangement, whilst not compromising selectivity. Without wishing to be held to any particular theory, it is believed that the inclusion of the mesopores has resulted in increased access of the substrates to the active sites, as well as the formation of additional active sites (silanols) that may participate in the reaction.

Reference Example 8: Synthesis and Characterization of Additional Hierarchical Porous AIPO Catalysts

[0163] Aluminum isopropoxide (6.807g, Aldrich) was added to a Teflon beaker with phosphoric acid (2.28ml, 85% in H2O, Aldrich) and water (10ml) and vigorously stirred for 1.5 hours until a homogeneous solution was formed. dimethyloctadecyl[(3-(trimethoxysilyl)propyl]ammonium chloride (DMOD) (1.2ml, 72% in H2O, Aldrich) was added drop wise, followed immediately by the addition of triethylamine (3.7ml, Aldrich) drop wise and then water (20ml). The resulting thicker solution was stirred for one hour. The metal precursors as shown in Table 4 were added drop wise and the gel was stirred for a further 1.5 hours.

[0164] A microporous analog was formed using the same method, but without the inclusion of the DMOD.

Table 4: Gel composition

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Gel Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP Co AIPO-5</td>
<td>1 Al: 1.3 P : 0.8 SDA : 0.1 DMOD : 50 H2O: 0.03 Co</td>
</tr>
<tr>
<td>HP Ti AIPO-5</td>
<td>1 Al: 1.3 P : 0.8 SDA : 0.1 DMOD : 50 H2O : 0.03 Ti</td>
</tr>
<tr>
<td>HP Co Ti AIPO-5</td>
<td>1 Al: 1.3 P : 0.8 SDA : 0.1 DMOD : 50 H2O: 0.03 Co : 0.03 Ti</td>
</tr>
</tbody>
</table>

[0165] The contents of the gel were divided between three 23 ml Teflon-lined stainless-steel autoclaves that were transferred to a pre heated fan assisted oven (WF-30 Lenton) at 200°C for 24 hours. The solid product from each autoclave was collected via filtration and washed with 500 ml of deionized water. The product was left to dry at 80°C overnight. The as-synthesized catalyst was calcined in a tube furnace under a flow of air at 550°C for 16 hours to produce a white solid.

[0166] The effect of different metal combinations within the multi-metallic hierarchically porous (HP) catalysts was investigated using an array of spectroscopic techniques. All the multi-metallic HP catalysts were synthesized using the same soft-templating technique, which employed the organosilane surfactant, dimethyloctadecyl[(3-(trimethoxyxysilyl)propyl]ammonium chloride (DMOD) to direct the formation of the mesopores and triethylamine to direct the formation of the micropores. DMOD was chosen as an appropriate surfactant owing to its silicon containing hydrophilic head and the high propensity for Si-O-Si and Si-O-Al bonds to form, therefore promoting the formation of mesopores throughout the AIPO framework. In order to assess the impact of different metal combinations on the intrinsic nature of the active site identical synthesis procedure was used for the catalysts. The catalysts will contain silicon in the framework too due to the nature of the synthesis.

[0167] As shown in the powder X-ray diffraction patterns illustrated in Figure 37, the various metal combinations, cobalt, titanium as well as cobalt and titanium, within the HP AIPO-5 framework did not result in any structural or phase imperfections and the intended crystalline AFI framework was yielded.

[0168] Figure 38A is an SEM image of HP Co AIPO-5, Figure 38B is an SEM image of HP Ti AIPO-5, and Figure 38C is an SEM image of HP Co Ti AIPO-5. As shown in Figures 38A-38C, scanning electron microscopy revealed the expected spherical AIPO-5 particles I the region of 5-30 microns further substantiating the successful synthesis of the AIPO-5 framework.

[0169] BET measurements were performed to assess the efficacy of our design strategy in the generation of hierarchically porous catalysts. Figure 39A illustrates the nitrogen adsorption isotherm for each catalyst. All the hierarchically porous samples exhibited a type IV isotherm, indicating the presence of mesopores within the catalyst.
The BJH adsorption pore distribution curves further demonstrated that all the HP catalysts contained mesopores that are approximately 40 Å in diameter. As shown in Table 5, all the HP catalysts had larger total surface areas and mesopore volumes than their microporous analogues, whilst still retaining similar microporous surface areas and micropore volumes. The BET data strongly indicates the successful incorporation of mesopores into the hierarchically porous frameworks.

In order to investigate the local coordination geometry of the Al(III), P(V) and Si(IV) sites MAS NMR was deployed. Figure 40A illustrates the 29Si MAS NMR of HP Co AIPO-5. Figure 40B illustrates the 29Si MAS NMR of HP Ti AIPO-5. Figure 40C illustrates the 29Si MAS NMR of HP Co Ti AIPO-5. The 29Si MAS NMR of the three hierarchically porous catalysts further confirmed the incorporation of the silicon into the framework due to the utilization of the organosilane in the synthesis procedure. The signals in the 29Si MAS NMR is broad for all three of the HP catalysts, which indicates that there is an element of silicon zoning, which would be expected due nature of the synthesis. Although the main peak observed for the HP catalysts was at about -90ppm, this is often assigned to isolated acidic Si(OAl)4 sites which are isolated sites formed via type II substitution. This is actually unusual for Si AIPO-5 frameworks; typically one would expect a much broader signal with a lower ppm near to -100ppm. Therefore this is very interesting catalytically and synthetically as the HP catalysts represent a way as to generate isolated silicon sites within an AFI aluminophosphates framework that are otherwise difficult to form.

To elucidate the nature of the cobalt and titanium metallic sites in the substituted HP AIPO-5 catalysts diffuse reflectance (DR) UV/vis was employed. Figure 41 illustrates the DR UV/vis spectra of the HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5. Diffuse reflectance UV Vis measurements enabled the molecular environments of the substituted cobalt and titanium ions within the AIPO framework to be investigated. The DR UV/vis of the reduced cobalt containing HP AIPOs have triplet bands in the visible region between 500 and 700nm which can be attributed to the d-d transitions of Co(II) ions in tetrahedral coordination. The DR UV-Vis spectrum of reduced HP Co Ti ALPO-5 and HP Ti AIPO-5 show one strong absorption band in the 200-250nm range due to tetrahedral Ti(IV) LMCT transitions with the framework oxygen ligands. The broad nature of this band indicates that the titanium isn’t purely tetrahedral. Rather, the titanium centres are likely to be a mix between the tetrahedral and octahedral Ti (IV) sites this is often commonly seen within titanium substituted AlPOs. Although it should be noted that the Ti(IV) band in the HP Co Ti AIPO-5 is sharper than in HP Ti AIPO-5, indicating that the Ti (IV) ions are more tetrahedral in nature in the cobalt containing catalyst. This phenomenon can be attributed to ‘support synergy’ in which a second metal can help direct the titanium into the framework and has been observed in the microporous analogues previously.

The isomorphous substitution of Co(II) via type I substitution and Ti(IV) via type II substitution will both lead to an acid site being generated as will the incorporation of the Si(IV), and the strength, type and quantity of these sites will be intimately related to the catalysts activity. Therefore FT-IR was utilised to probe the acidity of the hierarchically porous frameworks further, as provided in Figure 42. Figure 42 illustrates the FTIR spectra of the OH-stretching region for HP Co AIPO-5, HP Ti AIPO-5, and HP Co Ti AIPO-5. Direct observation of the O-H stretching region indicated that the spectra was very similar for all three of the catalysts. Each contained bands due to Al-OH and P-OH defects as well as bands owing to silicon incorporation into the AIPO framework. There was a band at about 3640cm⁻¹ in all three hierarchically porous frameworks that corresponds to Bronsted acid sites within the catalysts owing to the silicon being isomorphously substituted into the framework via type 2 or type 3 substitutions or a combination of both. There was also an additional band at 3750cm⁻¹, this is attributed to the silanol sites in the catalysts which originate from the calcination

Table 5: BET measurements for microporous and HP MII MIII AIPO-5 catalysts

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<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
<th>Mesopore and External Surface area (m²/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Mesopore volume (cm³/g)</th>
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<tr>
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<tr>
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<td>106.3</td>
<td>0.09</td>
<td>0.23</td>
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<td>288.8</td>
<td>115.56</td>
<td>0.07</td>
<td>0.35</td>
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</table>
of the surfactant in the mesopores. The FTIR data therefore indicates, as did the $^{29}$Si MAS NMR (see Figure 40A-40C), that the surfactant has been successfully incorporated into the frameworks.

[0174] FTIR spectroscopy coupled with the small basic CO probe molecule enabled the elucidation of the type and strength of acid sites present in the frameworks, as shown in Figures 43A-C. Figure 43A illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Co AlPO-5. Figure 43B illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Ti AlPO-5. Figure 43C illustrates the FTIR spectra of CO adsorbed at 80k on calcined HP Co Ti AlPO-5. Observation of the CO region of the FTIR spectra revealed that the cobalt containing catalysts (HP Co AlPO-5 and HP Co Ti AlPO-5) contained Lewis acid sites as well as Bronsted acid sites. The HP Ti AlPO-5 also had absorbance bands due to CO coordinated with both Lewis and Bronsted acid sites, although it was observed with much lower CO adsorption on Lewis acid sites compared to the cobalt containing samples, hence indicating that the HP Ti AlPO-5 has much less Lewis acidity than the cobalt containing frameworks.

[0175] Figures 44A-44C illustrate the FTIR spectra after the addition of 0.02cc, 0.08cc and 0.16cc, respectively, of CO adsorbed at 80K on calcined HP Co AlPO-5, HP Ti AlPO-5, and HP Co Ti AlPO-5. As shown in Figures 44A-44C and Table 6, in the OH region CO adsorption resulted in a shift of the Si-OH, P-OH and Si-OH-Al bands to lower frequency.

[0176] As shown in Figures 44A-44C and Table 6, at low CO coverage all samples showed a shifted Si-OH-Al band around $3365\text{cm}^{-1}$ in the hydroxyl region. This resulted in a band shift between 275 and $278\text{cm}^{-1}$ which is typical for a SAPO catalyst. The two cobalt-containing samples also had an additional band around $3235\text{cm}^{-1}$ with a shift of >$400\text{cm}^{-1}$ which is attributed to the CO interacting with stronger Bronsted acid sites. At higher CO coverage (0.08cc), the three catalysts had an additional shifted OH band around $3470\text{cm}^{-1}$ due to interaction of the CO with the P-OH defect groups. At even higher CO coverage (0.16cc) there is a small amount of attenuation of the Si-OH bands around $3745\text{cm}^{-1}$ for the three samples. The FTIR-CO revealed that the cobalt containing HP AlPO-5s contained considerable stronger and more acid sites than the HP Ti AlPO-5.

[0177] Figure 45 illustrates the TPD nitrogen adsorption results for HP Co AlPO-5, HP Ti AlPO-5, and HP Co Ti AlPO-5. Figure 45 further supports the observation above and indicates that the Cobalt containing catalysts have essentially identical acid site number and strength distributions, whereas the HP Ti AlPO-5 catalyst has significantly lower total acidity and fewer stronger sites. This is very revealing, as from $^{29}$Si NMR the local environmental of the silicon is essentially the same for the three catalysts (Figures 40A-40C) and from BET (Figures 39A and 39B) and SEM (Figure 38A-38C) the porosity and particle sizes were ascertained to be extremely similar. Therefore these differences in acid strength and type must be originating from the dopant metals, hence highlighting the real possibilities of tuning the active sites for particular reactions.

[0178] Figure 46 illustrates the results of a probe with a bulkier basic probe, collidine. As shown in Figure 46, the FTIR with a bulkier basic probe, collidine enabled the accessibility of the Bronsted acid sites as well as their strength and quantity to be assessed. Each catalyst was loaded with collidine and then heated to a certain temperature in order to investigate the strength of the acid sites. Observation of the hydroxyl region of the FTIR revealed that the collidine interacted with all the hydroxyl groups within all the catalysts and this resulted in the formation of a protonated species that has a N-H stretch around $3300\text{cm}^{-1}$. As the temperature of the sample with collidine was increased the collidine desorbed from the sample and very little remained after 450°C desorption. The behavior of the three HP catalysts was very similar. The total collidine adsorption is highest on the cobalt only HP catalyst and it also had the highest number of strong sites. The strength distribution was very similar for the two cobalt-containing samples, with a higher proportion of moderate sites compared to the titanium only sample.

[0179] By employing a range of spectroscopic techniques it was possible to ascertain the various strengths and type of acid sites within the HP AlPOs. Given that the samples had analogous porosity and silicon environments it would be reasonable to assume that the differences in acidity are due to the cobalt and titanium isomorphously substituted into the framework. In order to investigate these catalysts further they were tested in catalytic reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bridging OH</th>
<th>CO Area (AU) (0.18cc added)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before CO</td>
<td>After CO</td>
</tr>
<tr>
<td>HP Co AlPO-5</td>
<td>3644</td>
<td>3366</td>
</tr>
<tr>
<td>HP Ti AlPO-5</td>
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<td>3364</td>
</tr>
<tr>
<td>HP Co Ti AlPO-5</td>
<td>3642</td>
<td>3364</td>
</tr>
</tbody>
</table>
Example 9: Beckmann rearrangement of Cyclohexanone oxime

[0180] The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam was performed in a three necked round bottom flask under nitrogen. Benzonitrile (20ml) was added to the flask with 0.1g of cyclohexanone oxime, 0.1g of chlorobenzene (internal standard) and 0.1g of catalyst. The reaction was performed at 130°C and aliquots were taken frequently in order to monitor the course of the reaction. The solutions were centrifuged and analyzed by Perkin Elmer Calirus 480 GC using an Elite-5 column and Flame Ionization Detector. The products were identified and quantified by using chlorobenzene as an internal standard and employing the calibration method.

[0181] It was ascertained from the spectroscopic investigations that all three HP catalysts contained Bronsted acid sites, with the cobalt containing sites also having some Lewis acidity. Therefore the industrially significant Beckmann rearrangement was chosen as the probe reaction to investigate the catalysts active sites further. This transformation is used to convert cyclic oximes into the lactam monomeric building blocks for Nylon synthesis. It is well known that weak Bronsted acid sites are preferred for this reaction with stronger sites and Lewis acid sites often promoting the formation of the unwanted ketone. Therefore the nature of the active sites within the HP AlPOs should affect their catalytic activity and selectivity.

[0182] All three of the HP AlPO catalysts were active in the liquid phase Beckmann rearrangement. Figure 47A illustrates the percent conversion, percent selectivity, and percent yield for the liquid phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam for various catalysts. The reaction was performed using 0.1 g cyclohexanone oxime, 0.1 g catalyst, 0.1 g chlorobenzene (IS), 20 ml anhydrous PhCN, 130°C under nitrogen for 7 hours. The HP Ti AlPO-5 was 100% selective towards the desired product, ε-caprolactam. Both HP Co AlPO5 and HP Co Ti AlPO-5 produced cyclohexanone as a by-product. Without wishing to be held to any particular theory, the formation of cyclohexanone is thought to be due to Lewis acidity as well as stronger acid sites being present, which both HP Co AlPO-5 and HP Co Ti AlPO-5 have (Figures 40A-40C). Interestingly though the HP Co Ti AlPO-5 is more selective than the HP Co AlPO-5 even though both have near identical acid strength and quantity. The HP Co Ti AlPO-5 also has the highest conversion at 71% and hence the largest yield of ε-caprolactam at 39%, with the HP Ti AlPO-5 that has 100% selectivity with a lower yield of 29%. These differences between the two catalysts could be due to synergy between the Co and Ti sites. From DR UV/Vis (Figure 41) it was speculated that the titanium was more tetrahedral in nature in the bimetallic form laurolactam, likewise HP AlPO-5 was also active. Although they both were not as successful as the multi-metallic far more active than the microporous catalysts Cylcododecanone oxime (0.9nm) is larger than the micropores of AIPO-5 (0.7nm), therefore seeing as the microporous catalysts are active in this rearrangement it is likely that both external and internal sites are active for this reaction. The hierarchically porous catalysts will have both external and internal sites accessible to the substrate leading to extremely high conversions after just two hours (92% for HP Ti AlPO-5) whereas in the case of the microporous analogue only the external sites will be available and hence a lower conversion is observed (just 24% for Ti AlPO-5). In this reaction the hierarchically porous catalysts all have very high conversions 81-92% with 100% selectivity. In order to elucidate the origin for the high conversions both MCM 41 and HP AIPO-5 were tested in this reaction. Unlike in the rearrangement of cyclohexanone oxime, MCM 41 was active in this reaction and was able to form laurolactam, likewise HP AlPO-5 was also active. Although they both were not as successful as the multi-metallic HP AIPO-5, therefore highlighting the importance of the metals within the framework to subtly tune the intrinsic nature of the active site for a particular reaction.

[0185] While the present disclosure is primarily directed to Beckmann rearrangement of cyclohexanone oxime, cyclooctanone oxime, and cyclododecanone oxime to their corresponding lactams, it should be understood that the features disclosed herein have application to the production of other lactams and other monomers.

[0186] As shown in Figure 47A, the hierarchical porous catalysts demonstrate high activity and improved selectivities in catalytic performance.

[0184] Referring next to Figure 47B, in order to further test the efficacy of the HP catalysts a larger substrate, cyclooctanone oxime (0.9nm) was utilized in the Beckmann rearrangement to laurolactam, precursor to industrially significant Nylon 12. The reaction carried out was the liquid phase Beckmann rearrangement of cyclododecanone oxime to laurolactam under reaction conditions of 0.1 g cyclododecanone oxime, 0.1 g catalyst, 0.1 g chlorobenzene (IS), 20 ml anhydrous PhCN, 130°C under nitrogen, for 2 hours. As shown in Figure 47B, the hierarchically porous catalysts were far more active than the microporous catalysts Cyclododecanone oxime (0.9nm) is larger than the micropores of AlPO-5 (0.7nm), therefore seeing as the microporous catalysts are active in this rearrangement it is likely that both external and internal sites are active for this reaction. The hierarchically porous catalysts will have both external and internal sites accessible to the substrate leading to extremely high conversions after just two hours (92% for HP Ti AlPO-5) whereas in the case of the microporous analogue only the external sites will be available and hence a lower conversion is observed (just 24% for Ti AlPO-5). In this reaction the hierarchically porous catalysts all have very high conversions 81-92% with 100% selectivity. In order to elucidate the origin for the high conversions both MCM 41 and HP AIPO-5 were tested in this reaction. Unlike in the rearrangement of cyclohexanone oxime, MCM 41 was active in this reaction and was able to form laurolactam, likewise HP AlPO-5 was also active. Although they both were not as successful as the multi-metallic HP AIPO-5, therefore highlighting the importance of the metals within the framework to subtly tune the intrinsic nature of the active site for a particular reaction.

[0185] While the present disclosure is primarily directed to Beckmann rearrangement of cyclohexanone oxime, cyclooctanone oxime, and cyclododecanone oxime to their corresponding lactams, it should be understood that the features disclosed herein have application to the production of other lactams and other monomers.

[0186] While this invention has been described as relative to exemplary designs, the present invention may be further modified within the scope of this disclosure.

Claims

1. A method of performing a Beckmann rearrangement reaction comprising the step of:
reacting an oxime in the presence of a catalyst to produce a lactam, said catalyst comprising a hierarchical porous aluminophosphate comprising a microporous framework and a mesoporous framework, wherein the catalyst is a hierarchical porous silicoaluminophosphate catalyst selected from the group consisting of: SAPO-5, SAPO-34, SAPO-37, Co AIPO-5, Ti AIPO-5, and Co Ti AIPO-5,

wherein the mesoporous framework has a pore diameter from 20 A to 50 A, and wherein the microporous framework has a pore diameter from 3 A to 10 A.

2. The method of claim 1, wherein the oxime is selected from cyclohexanone oxime, cyclooctanone oxime, and cycloodecanone oxime.

3. The method of claim 1, wherein the oxime is selected from 4-hydroxy acetophenone oxime and oximes formed from acetophenone, butyaldehyde, cyclopentanone, cycloheptanone, cyclooctanone, and benzaldehyde.

4. The method of claim 1, wherein the lactam is selected from the group consisting of: ε-caprolactam ω-laurolactam 11-undecanolactam, 2-Pyrrolidone, and 2-Piperidone.

5. The method of claim 1 wherein the oxime is cyclohexanone oxime, and the lactam is ε-caprolactam.

6. The method of claim 1, wherein the oxime is cyclooctanone oxime, and the lactam is ω-laurolactam.

7. The method of claim 1, wherein the oxime is cyclooctanone oxime and the lactam is caprylolactam.

8. The method of claim 1, wherein the hierarchical catalyst includes a plurality of mesopores with a pore diameter of 20 A to 40 A.

9. The method of claim 1, wherein the reaction is a gas phase reaction and is performed at a temperature below 350°C, preferably the reaction is performed at a temperature from about 130°C to about 300°C.

10. The method of claim 1, wherein the reaction is a liquid phase reaction and is performed at a temperature beneath 250°C, preferably the reaction is performed at a temperature from about 100°C to about 170°C.

11. The method of claim 1, wherein the reaction is performed in the absence of a solvent.

12. The method of claim 1, wherein the reaction is performed in the presence of a solvent.

13. The method of claim 12, wherein the solvent is an organic nitrile of formula:

\[ R^1-CN \]

wherein \( R^1 \) represents \( C_1-C_8 \)-alkyl, \( C_1-C_8 \)-alkenyl, \( C_1-C_8 \)-alkynyl, \( C_3-C_8 \)-cycloalkyl; \( C_3-C_8 \)-arylalkyl including a \( C_6 \) aromatic ring, preferably wherein the organic nitrile is selected from acetonitrile, benzonitrile and mixtures thereof; or aromatic compounds of formula:

\[ R^2-Ar \]

wherein \( Ar \) is an aromatic ring and \( R^2 \) represents H, CH\(_3\), F, Cl, or Br, and \( Ar \) may be substituted with one or more \( R^2 \) groups, preferably wherein the aromatic compound is selected from benzene, toluene, xylene, and chlorobenzene; or

water and alcohols of formula:

\[ R^3-OH \]

wherein \( R^3 \) represents hydrogen, \( C_1-C_8 \)-alkyl, \( C_1-C_8 \)-alkenyl, \( C_1-C_8 \)-alkynyl, \( C_3-C_8 \)-cycloalkyl; \( C_3-C_8 \)-arylalkyl, preferably wherein the alcohol is selected from methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, iso-butanol, tert-butanol, n-amyl alcohol, n-hexanol, phenol, and mixtures thereof.
Patentansprüche

1. Verfahren zur Durchführung einer Beckmann-Umlagerungsreaktion, das den folgenden Schritt umfasst:
   Umsetzen eines Oxims in Gegenwart eines Katalysators zur Herstellung eines Lactams, wobei der Katalysator ein hierarchisches poröses Aluminophosphat mit einem mikroporösen Gerüst und einem mesoporösen Gerüst umfasst, wobei es sich bei dem Katalysator um einen hierarchischen porösen Silicoaluminophosphatkatalysator aus der Gruppe bestehend aus SAPO-5, SAPO-34, SAPO-37, Co-AlPO-5, Ti-AlPO-5 und Co-Ti-AlPO-5 handelt, wobei das mesoporöse Gerüst einen Porendurchmesser von 20 Å bis 50 Å aufweist und wobei das mikroporöse Gerüst einen Porendurchmesser von 3 Å bis 10 Å aufweist.

2. Verfahren nach Anspruch 1, bei dem das Oxim aus Cyclohexanonoxim, Cyclooctanoxonoxim und Cyclododecanonoxim ausgewählt wird.

3. Verfahren nach Anspruch 1, bei dem das Oxim aus 4-Hydroxyacetophenonoxim und aus Acetophenon, Butyraldehyde, Cyclopentanon, Cycloheptanon und Benzaldehyd gebildeten Oximen ausgewählt wird.

4. Verfahren nach Anspruch 1, bei dem das Lactam aus der Gruppe bestehend aus ε-Caprolactam, ω-Laurolactam, 11-Undecanlactam, 2-Pyrrolidon und 2-Piperidon ausgewählt wird.

5. Verfahren nach Anspruch 1, bei dem es sich bei dem Oxim um Cyclohexanonoxim handelt und es sich bei dem Lactam um ε-Caprolactam handelt.

6. Verfahren nach Anspruch 1, bei dem es sich bei dem Oxim um Cyclooctanoxonoxim handelt und es sich bei dem Lactam um ε-Caprolactam handelt.

7. Verfahren nach Anspruch 1, bei dem es sich bei dem Oxim um Cyclooctanoxonoxim handelt und es sich bei dem Lactam um ω-Laurolactam handelt.


9. Verfahren nach Anspruch 1, bei dem die Reaktion eine Gasphasenreaktion ist und bei einer Temperatur unter 350 °C und vorzugsweise bei einer Temperatur von etwa 130 °C bis etwa 300 °C durchgeführt wird.

10. Verfahren nach Anspruch 1, bei dem die Reaktion eine Flüssigphasenreaktion ist und bei einer Temperatur unter 250 °C und vorzugsweise bei einer Temperatur von etwa 100 °C bis etwa 170 °C durchgeführt wird.

11. Verfahren nach Anspruch 1, bei dem die Reaktion in Abwesenheit eines Lösungsmittels durchgeführt wird.

12. Verfahren nach Anspruch 1, bei dem die Reaktion in Gegenwart eines Lösungsmittels durchgeführt wird.

13. Verfahren nach Anspruch 12, bei dem es sich bei dem Lösungsmittel um ein organisches Nitril der Formel: R₁-CN wobei R₁ für C₁-C₈-Alkyl, C₁-C₈-Alkenyl, C₁-C₈-Alkinyl, C₃-C₈-Cycloalkyl oder C₃-C₈-Araalkyl mit einem aromatischen C₆-Ring steht, wobei das organische Nitril vorzugsweise aus Acetonitril, Benzonitril und Mischungen davon ausgewählt wird; oder aromatische Verbindungen der Formel: R₂-Ar

wobei Ar ein aromatischer Ring ist und $R^2$ für H, CH₃, F, Cl oder Br steht und Ar durch eine oder mehrere $R^2$-Gruppen substituiert sein kann, wobei die aromatische Verbindung vorzugsweise aus Benzol, Tolul, Xylol und Chlorbenzol ausgewählt wird; oder Wasser und Alkohole der Formel: R₃-OH
Revendications

1. Procédé de conduite d’une réaction de réarrangement de Beckmann comprenant l’étape de :
   réaction d’une oxime en présence d’un catalyseur pour produire un lactame, ledit catalyseur comprenant un
   alumino(phosphate poreux hiérarchique comprenant une structure microporeuse et une structure mésoporeuse,
   dans lequel le catalyseur est un catalyseur de silicoalumino(phosphate poreux hiérarchique choisi dans le groupe
   constitué de : SAPO-5, SAPO-34, SAPO-37, Co AIPO-5, Ti AIPO-5, et Co Ti AIPO-5,
   dans lequel la structure mésoporeuse a un diamètre de pore de 20 Å à 50 Å, et
   dans lequel la structure microporeuse a un diamètre de pore de 3 Å à 10 Å.

2. Procédé selon la revendication 1, dans lequel l’oxime est choisie parmi la cyclohexanone oxime, la cyclooctanone
   oxime et la cyclo Dodécanone oxime.

3. Procédé selon la revendication 1, dans lequel l’oxime est choisie parmi la 4-hydroxyacétophénone oxime et des
   oximes formées à partir d’acétophénone, de butyraldéhyde, de cyclopentanone, de cycloheptanone, de cycloocta-
   nol et de benzaldéhyde.

4. Procédé selon la revendication 1, dans lequel le lactame est choisi dans le groupe constitué de : ε-caprolactame,
   ω-laurolactame, 11-undécanolactame, 2-pyrrolidone et 2-pipéridone.

5. Procédé selon la revendication 1, dans lequel l’oxime est la cyclohexanone oxime, et le lactame est le ε-caprolactame.

6. Procédé selon la revendication 1, dans lequel l’oxime est la cyclooctanone oxime, et le lactame est le ω-lauro-
   lactame.

7. Procédé selon la revendication 1, dans lequel l’oxime est la cyclooctanone oxime et le lactame est le capryl lactame.

8. Procédé selon la revendication 1, dans lequel le catalyseur hiérarchique comprend une pluralité de mésopores
   ayant un diamètre de pore de 20 Å à 40 Å.

9. Procédé selon la revendication 1, dans lequel la réaction est une réaction en phase gazeuse et est conduite à une
   température inférieure à 350 °C, de préférence la réaction est conduite à une température d’environ 130 °C à environ
   300 °C.

10. Procédé selon la revendication 1, dans lequel la réaction est une réaction en phase liquide et est conduite à une
    température inférieure à 250 °C, de préférence la réaction est conduite à une température d’environ 100 °C à environ
    170 °C.

11. Procédé selon la revendication 1, dans lequel la réaction est conduite en l’absence d’un solvant.

12. Procédé selon la revendication 1, dans lequel la réaction est conduite en présence d’un solvant.

13. Procédé selon la revendication 12, dans lequel le solvant est un nitrile organique de formule :

    \[ R^{1} \text{-CN} \]

dans laquelle \( R^{1} \) représente alkyle en C1-C8, alcényle en C1-C8, alcynyle en C1-C8, cycloalkyle en C3-C8 ; aralkyle
en C3-C8 comprenant un cycle aromatique en C6, de préférence dans lequel le nitrile organique est choisi parmi
l’acétonitrile, le benzonitrile et des mélanges de ceux-ci ; ou

14. Procédé selon la revendication 12, dans lequel le solvant est un nitrile organique de formule :

    \[ R^{1} \text{-CN} \]

dans laquelle \( R^{1} \) représente alkyle en C1-C8, alcényle en C1-C8, alcynyle en C1-C8, cycloalkyle en C3-C8 ; aralkyle
en C3-C8 comprenant un cycle aromatique en C6, de préférence dans lequel le nitrile organique est choisi parmi
l’acétonitrile, le benzonitrile et des mélanges de ceux-ci ; ou
R²-Ar
dans laquelle Ar est un cycle aromatique et R² représente H, CH₃, F, Cl ou Br, et Ar peut être substitué par un ou plusieurs groupes R², de préférence dans laquelle le composé aromatique est choisi parmi le benzène, le toluène, le xylène et le chlorobenzène ; ou
l’eau et des alcools de formule :
R³-OH
dans laquelle R³ représente hydrogène, alkyle en C₁-C₈, alcényle en C₁-C₈, alcynyle en C₁-C₈, cycloalkyle en C₃-C₈ ; aralkyle en C₃-C₈, de préférence dans laquelle l’alcool est choisi parmi le méthanol, l’éthanol, le n-propanol, l’iso-propanol, le n-butanol, le sec-butanol, l’iso-butanol, le tert-butanol, l’alcool n-amylique, le n-hexanol, le phénol, et des mélanges de ceux-ci.
Figure 2

Zeolites → 102

SAPOs → 104

Mesoporous Silica → 106

Hierarchical SAPO → 114

Micropores → 110

Mesopores → 112

114
Figure 3
Possible active sites present in the hierarchical SAPOs

**Micropore:**
Type II substitution

**Mesopores:**
Silanols from combustion of surfactant Brønsted acids via type II substitution

Figure 5
Figure 6
Figure 7C
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### SAPO-5

Figure 8A

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### HP SAPO-5

Figure 8B
### Figure 9A

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### Figure 9B

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**SAPO-34**

**HP SAPO-34**
Figure 10C
Figure 13

HP SAPO-34

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HP SAPO-5

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Figure 15

HP SAPO-5
Figure 16

HP SAPO-5
Figure 17

HP SAPO-34
Figure 18

HP SAPO-34
Figure 20C

![Graph showing caprolactam yield over time for HP SAPO 5 and SAPO 5. The graph includes a linear trend line for SAPO 5, indicating a decrease in caprolactam yield as time increases.](image-url)
Figure 20F

Caprolactam Yield (%) vs Time (minute)

- HP SAPO 34
- SAPO 34
Figure 21C

Caprylolactam Yield (%) vs. Time (minutes)

- SAPO 5
- HP SAPO 5
Figure 21F

![Graph showing Caprylactam Yield over Time](image)

- **HP SAPO 34**
- **SAPO 34**

Caprylactam Yield (%) vs. Time (minutes)
Figure 21l

![Graph showing the yield of caprolactam over time with two different catalysts: H ZSM 5 and MCM-41. The graph plots Caprolactam Yield (%) against Time (minutes).]
Figure 22A

HP SAPO 5 (0.2g)

WHSV = 0.79 hr⁻¹
10wt% solution of oxime in EtOH
33.3 ml/min He

Figure 22B

Conversion (%)

Time (minutes)

Figure 22C

Selectivity (%)

Time (minutes)
Figure 23A

NOH

HP SAPO 34 (0.2g)

WHSV= 0.79hr⁻¹
10wt% solution of oxime in EtOH
33.3 ml/min He

Figure 23B

Cyclohexanone oxime conversion (%) vs. time (minutes)

- 300°C
- 325°C
- 350°C
- 400°C

Figure 23C

Caprolactam selectivity (%) vs. time (minutes)

- 350°C
- 400°C
- 300°C
- 325°C
Figure 24A

HP SAPO 5 (0.2g)

WHSV= 0.79 hr⁻¹
10 wt% solution of oxime in EtOH
33.3 ml/min He

Figure 24B

Oxime Conversion (%)

- WHSV = 1.6 hr⁻¹
- WHSV = 0.8 hr⁻¹

Time (Minutes)

Figure 24C

Caprolactam Selectivity (%)

- WHSV = 0.8 hr⁻¹
- WHSV = 1.6 hr⁻¹

Time (Minutes)
Figure 25A

NOH

HP SAPO 34 (0.2g)

10wt% solution of oxime in EtOH

33.3 ml/min He

Figure 25B

Oxime Conversion (%)

WHSV = 1.6 hr\(^{-1}\)

WHSV = 0.8 hr\(^{-1}\)

Time (Minutes)

Figure 25C

Caprolactam Selectivity (%)

WHSV = 0.8 hr\(^{-1}\)

WHSV = 1.6 hr\(^{-1}\)

Time (minutes)
Liquid Beckmann Rearrangement: Cyclododecanone Oxime

130°C, PhCN (20ml), N₂, reflux, 7 hours, 0.1g catalyst, 0.1g oxime

Selectivity was 100% for all

- ◆ SAPO 5
- HP SAPO 5
- HP SAPO 34
- SAPO 34
- HP SAPO 37
- ◇ SAPO 37

Figure 26
Liquid Phase Beckmann rearrangement of cyclododecanone oxime with HP SAPO 5: Different quantities of catalyst

Selectivities were all 100%
Liquid Phase Beckmann rearrangement of cyclododecanone oxime with HP SAPO 34: Different quantities of catalyst

Selectivities were all 100%

- 0.1g oxime: 0.1g catalyst
- 0.1g oxime: 0.05g catalyst
- 0.1g oxime: 0.02g catalyst

Figure 27B
Liquid Phase Beckmann rearrangement of cyclododecanone oxime with HP SAPO 37: Different quantities of catalyst

Selectivities were all 100%

- 0.1g oxime: 0.1g catalyst
- 0.1g oxime: 0.05g catalyst
- 0.1g oxime: 0.02g catalyst

Figure 27C
$^{27}$Al MAS NMR spectra of SAPO-5

Figure 29A

$^{27}$Al MAS NMR spectra of HP SAPO-5

Figure 29B
$^{31}$P MAS NMR spectra of SAPO-5

Figure 29C

$^{31}$P MAS NMR spectra of HP SAPO-5

Figure 29D
$^{29}$Si MAS NMR spectra of SAPO-5 and HP SAPO-5

Figure 29E
$^{27}$Al MAS NMR spectra of SAPO-34

Figure 30A

$^{27}$Al MAS NMR spectra of HP SAPO-34

Figure 30B
$^{31}$P MAS NMR spectra of SAPO-34

$-29.41$

Figure 30C

$^{31}$P MAS NMR spectra of HP SAPO-34

$-29.26$

Figure 30D
$^{29}$Si MAS NMR spectra of SAPO-34 and HP SAPO-34

Figure 30E
$^{27}\text{Al}$ MAS NMR spectra of SAPO-37

-34.1 ppm
7.5 ppm

Figure 31A

$^{31}\text{P}$ MAS NMR spectra of HP SAPO-37

-26.8 ppm

Figure 31B
$^{29}$Si MAS NMR spectra of HP SAPO-37

Figure 31C
Figure 32C

Hydroxyl Region IR Spectra of SAPO Samples After Pretreatment

Absorbance

4000 3800 3600 3400 3200 3000
Wavenumber (cm⁻¹)

He 550°C 2 Hrs
SI-OH
SI-OH/Al
P-OH/Al
H-bonded OH
SAPO-34 HP
SAPO-5 HP
Normalized to 10 mg pellet
Figure 33C

NH₃-Temperature Programmed Desorption:
Pretreated in O₂/He at 10 C/min to 550°C for 120 min.
Desorption at 10 C/min to 650°C for 40 min.
HP SAPO-5

Figure 34A

HP SAPO-34

Figure 34B
pXRD

HP Co AlPO 5
HP Ti AlPO 5
HP Co Ti AlPO 5

2 theta

Figure 37
Figure 38A

Figure 38B

Figure 38C
BET isotherm

Volume Adsorbed (mL g\(^{-1}\))

Relative Pressure (\(P/P_0\))

Figure 39A
BJH adsorption pore size distribution curve

Figure 39B
Figure 40A

HP Co AlPO 5

$^{29}\text{Si/ppm}$

-91 ppm
-89 ppm

HP Ti AIPO 5

$^{29}\text{Si/ppm}$

Figure 40B
-90 ppm - 94 ppm

HP Co Ti AlPO 5

$^{29}\text{Si}/\text{ppm}$

Figure 40C
Figure 41
FTIR OH region

Figure 42
Figure 43A

FTIR-CO HP Co AlPO 5 (CO region)

Increasing strength

Absorbance

2240 2220 2200 2180 2160 2140 2120 2100

Wavenumber (cm⁻¹)

Increasing CO Coverage

Figure 43B

FTIR-CO HP Ti AlPO 5 (CO region)

Increasing strength

Absorbance

2240 2220 2200 2180 2160 2140 2120 2100

Wavenumber (cm⁻¹)

Increasing CO Coverage

Figure 43C

FTIR-CO HP Co Ti AlPO 5 (CO region)

Increasing strength

Absorbance

2240 2220 2200 2180 2160 2140 2120 2100

Wavenumber (cm⁻¹)

Increasing CO Coverage
FTIR-CO Difference Spectra (OH region)

Figure 44A

After 0.08cc CO addition

Figure 44B

After 0.16cc CO addition

Figure 44C
TPD-NH₃

- HP Co AlPO 5
- HP Ti AlPO 5
- HP Co Ti AlPO 5

Figure 45
FTIR-Collidine Desorption

![Bar chart showing Brønsted (Area/mg) for HP Co AIPO 5, HP Ti AIPO 5, and HP Co Ti AIPO 5 at 150°C, 450°C, and 300°C.]

Figure 46
Figure 47A

\[
\begin{align*}
\text{NOH} & \quad \rightarrow \quad \text{N} \quad \text{O} \\
\text{130°C,} & \quad \text{2 hours,} \\
\text{PhCN (20ml)} & \quad \text{0.1g catalyst, 0.1g oxime}
\end{align*}
\]
Liquid phase Beckman rearrangement of cyclododecanone oxime

Conversion  Selectivity  Yield
REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4440871 A, Lok [0052]
- US 8772476 B, Levy [0052]

Non-patent literature cited in the description

- M. E. POTTER et al. Role of Isolated Acid Sites and Influence of Pore Diameter in the Low-Temperature Dehydration of Ethanol. ACS Catal., vol. 4 (11), 4161-4169 [0052]