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Declarations under Rule 4.17:

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(54) Title: PROCESS FOR MANUFACTURE OF MOLECULAR SIEVES

(57) Abstract: Small particle size silicoaluminophosphate molecular sieves are obtained by providing the source of the silicon in the form of a basic organic solution.

PROCESS FOR MANUFACTURE OF MOLECULAR SIEVES

This invention relates to molecular sieves and processes for their manufacture. More especially it relates to a variation in the preparation of synthesis mixtures to control product characteristics. The invention relates primarily to the manufacture of phosphorus-containing molecular sieves, especially silicoaluminophosphates.

In U.S. Patent No. 4 440 871, the preparation of a number of phosphorus-containing molecular sieves is described.

The patent particularly describes processes for the manufacture of numerous crystalline microporous silicoaluminophosphates (SAPO's) including SAPO-34, employing sources of silicon (e.g., a silica sol), aluminium (e.g., hydrated aluminium oxide), and phosphorus (e.g., orthophosphoric acid), and an organic template, for example tetraethylammonium hydroxide (TEAOH), isopropylamine ($iPrNH_2$) or di-n-propylamine (DPA). The patent, the disclosure of which is incorporated by reference herein, gives X-ray diffraction data for the SAPO's and describes their utilities in catalysis and absorption.

International Application WO 00/06493 describes obtaining phosphorus-containing molecular sieves of lower particle size and narrower size distribution by agitation, e.g., stirring or tumbling.

EP-A-541 915 is concerned with the conversion of methanol to olefins (MTO), especially light (C_2 to C_4) olefins using an aluminophosphate crystalline molecular

sieve catalyst. The specification describes the advantages of small particle size catalysts in MTO processes, and provides a process for facilitating the manufacture of a small particle size material by stirring the synthesis mixture, producing SAPO-34 of median particle diameters, expressed as a mass distribution, in the range of about 0.6 to 1.4 μm.

EP-A-185 525 describes a process in which SAPO-37 is manufactured using a two-phase synthesis mixture. In an example there are used an aqueous phase containing phosphoric acid, alumina, and tetraethyl and tetrapropyl ammonium hydroxides as organic templates, and an organic phase comprising tetraethyl orthosilicate in hexanol, a solvent immiscible with water. In a comparative example, the silicon source, silica (Hisil), is dispersed in the tetrapropylammonium hydroxide.

International Application WO 01/36328 describes a process in which a metalloaluminophosphate molecular sieve is manufactured using an aqueous synthesis mixture comprising a template, sources of the elements essential to the structure of the sieve and an organic solvent miscible with water, the purpose of the solvent being to solubilize the source of the metal in the aqueous synthesis mixture. When the metal is silicon, the source may be a tetraalkyl orthosilicate.

The present invention is based on the observation that if the silicon-providing component is dissolved in an organic base prior to its incorporation in the synthesis mixture the resulting silicoaluminophosphate molecular sieve has a particle size smaller than that obtained from an otherwise identical synthesis

procedure in which the silicon-providing component is added directly or is merely dispersed in another component of the synthesis mixture.

The present invention accordingly provides a process for the manufacture of a silicoaluminophosphate crystalline molecular sieve which comprises providing sources of aluminium, of phosphorus and of silicon, the source of silicon being a solution of the silicon component in a water-miscible liquid organic base or in an aqueous solution of a solid organic base, forming a synthesis mixture from said sources and any other material necessary to form the molecular sieve, and treating the synthesis mixture for a period and at a temperature appropriate for the manufacture of the molecular sieve.

Crystalline molecular sieves obtainable by the process of the invention include those of the LEV structure type, e.g., SAPO-35, and those of the CHA structure type, e.g., SAPO-34 and 47. An especially preferred silicoaluminophosphate is SAPO-34.

The invention also provides a crystalline silico aluminophosphate molecular sieve, especially SAPO-34, the mean particle size of the molecular sieve being at most 400 nm, advantageously at most 200 nm, preferably at most 100 nm, and most preferably at most 50 nm. The molecular sieve is advantageously one obtainable by, and preferably is obtained by, the process of the invention. The mean particle size is measured by inspection of scanning electron micrographs (SEM's), the largest dimension of each particle being taken.

The invention especially provides SAPO-34 the particle size of which is such that at least 50%, and

preferably at least 90%, of the crystals by number are smaller than 100 nm. Preferably at least 50% of the crystals are smaller than 50 nm.

The components of the synthesis mixture used in the present invention are typically those known in the art or as described in the literature as suitable for the production of the molecular sieve, as are the conditions of the hydrothermal treatment, except for the dissolution of the silicon source in the organic base.

The liquid in which the silicon source is dissolved is conveniently a liquid organic base (which may be in admixture with water) or an aqueous solution of a normally solid organic base that is being used as a template in the synthesis of the crystalline molecular sieve. Other organic bases may be used, provided that they do not interfere with the structure directing properties of the organic base being used as template. Conveniently, any template that is difficultly soluble in water may be mixed with (if liquid) or dissolved in (if solid) the basic organic solvent. Heating may be necessary to effect solution of the silicon source.

Advantageously, all the silicon source is dissolved in the solvent.

Although the invention is not to be regarded as limited by any theory, it is believed that the reduction in product particle size achieved by the process of the invention may be attributable to the predissolution of the silicon source providing an increased number of nucleation sites from commencement

of molecular sieve crystal formation in the synthesis mixture.

In general, the treatment of the synthesis mixture to yield the desired crystalline molecular sieve, usually termed hydrothermal treatment, is advantageously carried out under autogenous pressure, for example in an autoclave, for example a stainless steel autoclave which may, if desired, be ptfe-lined. The treatment may, for example, be carried out at a temperature within the range of from 50, advantageously from 90, especially 120, to 250°C, depending on the molecular sieve being made. The treatment may, for example, be carried out for a period within the range of from 1 to 200 hours, preferably up to 100 hours, again depending on the molecular sieve being formed. The procedure may include an ageing period, either at room temperature or, preferably, at a moderately elevated temperature, before the hydrothermal treatment at more elevated temperature. The latter may include a period of gradual or stepwise variation in temperature.

As source for the phosphorus in the synthesis mixture, there may be mentioned phosphoric acid, organic phosphates, e.g., triethylphosphate, and aluminophosphates.

As source for aluminium in the synthesis mixture there may be mentioned alumina hydrate, alumina, sodium aluminate, pseudoboehmite, organic aluminium sources, e.g., alkoxides, for example, aluminium isopropoxide, aluminium phosphate.

As source for silicon there may be mentioned fumed silica, e.g., that sold under the trade name Aerosil; an aqueous colloidal suspension of silica, e.g., that

sold under the trade name Ludox AS40 or Ludox HS40; or organic silicon sources, e.g., a tetraalkyl orthosilicate, especially tetraethyl orthosilicate, although the invention is more especially of importance when the source of silicon is an inorganic source, it being understood that dissolution in the basic organic solvent may effect physical or chemical changes in the source as added.

In addition, the synthesis mixture will contain an organic structure-directing agent (template). In general, as indicated above, these compounds are generally organic bases, especially nitrogen-containing bases, more especially amines and quaternary ammonium compounds, used either singly or in mixtures.

As templates there may be mentioned, for example, tetraethyl ammonium compounds, cyclopentylamine, aminomethyl cyclohexane, piperidine, triethylamine, cyclohexylamine, trimethyl hydroxyethylamine, morpholine, dipropylamine (DPA), pyridine, isopropylamine and mixtures thereof. Preferred templates are triethylamine, cyclohexylamine, piperidine, pyridine, isopropylamine, tetraethyl ammonium compounds, dipropylamine, and mixtures thereof. The tetraethylammonium compounds include tetraethyl ammonium hydroxide (TEAOH), and tetraethyl ammonium phosphate, fluoride, bromide, chloride, and acetate. Preferred tetraethyl ammonium compounds are the hydroxide and the phosphate. The molecular sieve structure may be effectively controlled using combinations of templates.

In the manufacture of SAPO-34, it has proved advantageous to use a mixture of templates. For

example, a suitable template mixture is TEAOH, which is readily soluble in water, and DPA, which dissolves in water with some difficulty.

The treatment may be carried out with the vessel static or, preferably, with stirring or with rotating the vessel about a horizontal axis (tumbling). If desired, the synthesis mixture may be stirred or tumbled during an initial part of the heating stage, for example, from room temperature to an elevated, e.g., the final treatment, temperature, and be static for the remainder. Agitation generally produces a product with a smaller particle size and a narrower particle size distribution than static hydrothermal treatment.

A synthesis mixture for producing SAPO-34 according to the invention advantageously has a molar composition within the following ranges:

P_2O_5 : Al_2O_3		0.6 to 1.2 : 1,
	preferably	0.65 to 0.91 : 1
SiO_2 : Al_2O_3		0.01 to 0.5 : 1,
	preferably	0.1 to 0.5 : 1
H_2O : Al_2O_3		10 to 100 : 1

together with an organic template, advantageously tetraethylammonium hydroxide (TEAOH), dipropylamine (DPA), isopropylamine or morpholine, or a mixture of two or more such templates, in a proportion appropriate to yield SAPO-34. A preferred template mixture comprises TEAOH and DPA.

The invention also provides the use of a silicon source in the form of the silicon component in a solution, advantageously a basic organic solution, in the hydrothermal synthesis of a crystalline silicoaluminophosphate molecular sieve to control the particle size of the product.

The invention further provides the products of the processes and of the uses of the earlier aspects of the invention. The products, if required after cation exchange and/or calcining, have utility as catalyst precursors, catalysts, and separation and absorption media.

The molecular sieves of the present invention can be used as seeds in the manufacture of molecular sieves. The molecular sieves prepared by the method of the present invention may be used to seed the formation of molecular sieves of the same structure type or of a different structure type. They can be used to seed the formation of a zeolite or of a phosphorus-containing molecular sieve. The seeding of a phosphorus-containing synthesis mixture is described in above-mentioned International application WO 00/06493, the disclosure of which is incorporated herein by reference.

As used in this specification, the term "structure type" is used in the sense described in the Structure Type Atlas, Zeolites 17, 1996.

Accordingly, the present invention also relates to a process for manufacturing a molecular sieve, comprising (i) forming a synthesis mixture from a crystalline silicoaluminophosphate molecular sieve of the invention, sources of aluminium and of silicon, optionally a source of phosphorus and optionally one or

several structure-directing agents (templates) and any other material necessary to form the molecular sieve, and (ii) treating the synthesis mixture for a period and at a temperature appropriate for the manufacture of the molecular sieve.

In the embodiment where the silicoaluminophosphate molecular sieve of the invention is used as a seed, it is generally present in the synthesis mixture in a concentration of up to 10000 ppm, advantageously at most 3000 ppm, more advantageously at most 1500 ppm, and preferably at most 1000 ppm, more preferably at most 500 ppm, and most preferably at most 350 ppm, based on the total weight of the synthesis mixture. A minimum seeding level is generally 1 ppb (0.001 ppm), advantageously at least 0.1 ppm, more advantageously at least 1 ppm, and preferably at least 10 ppm, based on the total weight of the synthesis mixture. Advantageous ranges of proportions are from 1 ppm to 2000 ppm, preferably from 100 ppm to 1500 ppm, and most preferably from 100 ppm to 250 ppm.

The seeds are advantageously incorporated in the synthesis mixture in the form of a suspension, advantageously a colloidal suspension, advantageously in an aqueous medium, preferably water, or another liquid component of the synthesis mixture. As used herein, the term "colloidal", when used of a suspension, refers to one containing discrete finely divided particles, dispersed in a continuous liquid phase and preferably refers to a suspension that is stable, in the sense that no visible separation occurs or sediment forms, in a period sufficient for the use intended, advantageously for at least 10 hours, more

advantageously at least 20 hours, preferably at least 100 hours, and more preferably at least 500 hours, at ambient temperature (23°C).

When the silicoaluminophosphate molecular sieves of the invention are used as seeds, they have a mean particle size of at most 400 nm, advantageously at most 200 nm, preferably at most 100 nm, and most preferably at most 50 nm. Preferably, at least 50%, and more preferably at least 90%, of the crystals by number are smaller than 100 nm. Most preferably at least 50% of the crystals are smaller than 50 nm.

In one embodiment, the silicoaluminophosphate seeds are SAPO-34.

In another embodiment, the silicoaluminophosphate molecular sieve of the invention are especially useful in numerous hydrocarbon conversions, separations and absorptions. They may be used alone, or in admixture with other molecular sieves, in particulate form, supported or unsupported, or in the form of a supported layer, for example in the form of a membrane, for example as described in International Application WO 94/25151. Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, oligomerisation, isomerization, dewaxing, and hydrocracking (e.g., naphtha to light olefins, higher to lower molecular weight hydrocarbons, alkylation, transalkylation, disproportionation or isomerization of aromatics). Other conversions include the reaction of alcohols with olefins and the conversion of oxygenates to hydrocarbons, especially of methanol to olefins, especially light olefins. SAPO-34

produced by the process of the invention is especially suitable for this conversion.

Conversion of oxygenates may be carried out with the oxygenate, e.g., methanol, in the liquid or, preferably, the vapour phase, in batch or, preferably, continuous mode. When carried out in continuous mode, a weight hourly space velocity (WHSV), based on oxygenate, of advantageously 1 to 1000, preferably 1 to 100, $hour^{-1}$ may conveniently be used. An elevated temperature is generally required to obtain economic conversion rates, e.g., one between 300 and 600°C, preferably from 400 to 500°C, and more preferably about 450°C. The catalyst may be in a fixed bed, or a dynamic, e.g., fluidized or moving, bed.

The oxygenate feedstock may be mixed with a diluent, inert under the reaction conditions, e.g., argon, nitrogen, carbon dioxide, hydrogen, or steam. The concentration of methanol in the feedstream may vary widely, e.g., from 5 to 90 mole per cent of the feedstock. The pressure may vary within a wide range, e.g., from atmospheric to 500 kPa.

The following Examples, in which parts are by weight unless otherwise indicated, illustrate the invention. The source and purity of starting materials are those first given, unless indicated otherwise.

Example 1

This example illustrates the manufacture of SAPO-34 using the process of the invention.

A synthesis mixture was prepared from the following components in the proportions shown.

Component		Proportion
A	Colloidal silica (Ludox AS40) 40% in water	10.49
	TEAOH, (Eastern Chemical) 35% in water	97.88
B	Al_2O_3 (Condea Pural SB)	31.60
	water	119.20
C	H_3PO_4 (Acros), 85% in water	53.33
D	DPA (Fluka)	37.50

To the colloidal silica was added the TEAOH dropwise while stirring in a stainless steel autoclave. The mixture was heated over 2 hours to 100°C, and maintained at that temperature for 12 hours, the resulting solution forming Component A.

Al_2O_3 was placed in the bowl of a Kenwood mixer, and water added with stirring to form a slurry of Component B. Component C was then added, followed by Component A, and then Component D. The molar composition of the mixture was:

$$Al_2O_3 : P_2O_5 : 0.3\ SiO_2 : TEAOH : 1.59\ DPA : 52\ H_2O$$

The synthesis mixture was heated in a stainless steel autoclave over 2 hours to 175°C and maintained at that temperature without stirring for 96 hours. The solid product was recovered by centrifugation, washed four times with water to a conductivity of about 38 μS/cm and dried overnight at 120°C. XRD and SEM showed a pure SAPO-34 product with platelet crystals of uniform particle size; 50% by number of the crystals

were smaller than 700 nm, 10% were larger than 1.2 μm. Yield 13.9% based on the weight of the original synthesis mixture.

By way of comparison, a synthesis mixture of the same molar composition was prepared, but the silica and the TEAOH were added separately to the mixture. Hydrothermal treatment produced a pure SAPO-34 with cube-like crystals of varied dimensions between 0.5 μm and 20 μm; 50% by number of the crystals were smaller than 1.6 μm, 10% were greater than 3.8 μm.

Example 2

Following the procedure of Example 1, a synthesis mixture was prepared having the following molar composition:

$Al_2O_3 : P_2O_5 : 0.3\ SiO_2 : 2.00$ TEAOH $: 52\ H_2O$

i.e., the colloidal silica, Ludox AS40, was dissolved over the course of 12 hours in the 35% TEAOH aqueous solution at 100°C, but the synthesis mixture contained only TEAOH, no DPA, as template.

The synthesis mixture was heated in a stainless steel autoclave over 2 hours to 175°C, and maintained at that temperature for 96 hours without stirring. The crystalline solid product was recovered by centrifugation, washed four times to a conductivity of about 32 μS/cm and dried overnight at 120°C. The crystals were pure SAPO-34; 50% of the crystals by number were smaller than 50 nm, 10% were larger than 100 nm.

A similar synthesis mixture was prepared, and subjected to hydrothermal treatment but this time with stirring, at 170 rpm, for a period of 48 hours only. The crystals after washing and drying as above were of particle size somewhat less than 0.1 μm.

Two comparison experiments were carried out, each using a synthesis mixture of the same molar composition but adding the silica and the TEAOH separately to the mixture, one carrying out the hydrothermal treatment on a static mixture, the other with stirring at 170 rpm.

The static mixture was heated over 2 hours to 175°C, and maintained at that temperature for 96 hours; the stirred mixture was also heated over 2 hours to 175°C but maintained at that temperature for only 24 hours. In each case, the product was pure SAPO-34, of particle size about 1 μm.

Example 3

In this example, a synthesis mixture like that used in Example 1 was prepared, but only part of the silicon source was pre-dissolved. The H_3PO_4 was first added to the Al_2O_3/H_2O solution, followed by the addition of 96% of the silica, Ludox AS40, alone. Then the remainder of the Ludox AS40 was added, predissolved in the TEAOH (0.98 parts of Ludox AS140 in 223.43 parts TEAOH), followed by the DPA to give a synthesis mixture of molar composition:

$$Al_2O_3 : P_2O_5 : 0.3\ SiO_2 : TEAOH : 1.6\ DPA : 52\ H_2O$$

The synthesis mixture was heated in a stainless steel autoclave over 8 hours to 175°C and maintained at

that temperature without stirring for 96 hours. The solid product was recovered as described in Example 1. Most of the crystals were between 1 and 2 μm, with some larger than 10 μm, i.e., the product has smaller particle size than if all the silica is added separately, but larger than that if all is predissolved.

In further comparative experiments premixing of silica (Ludox AS40) with TEAOH, at room temperature with and without aging, but without dissolution of the silica in the basic aqueous-organic solvent, gave slow crystallization, resulting in poor yields, together with amorphous material, and broad crystal size distribution.

CLAIMS:

1. A process for the manufacture of a crystalline silicoaluminophosphate molecular sieve, which comprises: (a) providing sources of aluminium, of phosphorus and of silicon, the source of silicon being in solution with an organic base; (b) forming a synthesis mixture from said sources and any other material necessary to form the molecular sieve; and (c) treating the synthesis mixture for a period and at a temperature appropriate for the manufacture the molecular sieve.

2. A process as claimed in claim 1, wherein the source of silicon is a silicon component in solution in a water-miscible liquid organic base or a silicon component in an aqueous solution of a solid organic base.

3. A process as claimed in any of claims 1 or 2, wherein the said solution comprises a liquid organic base in admixture with water.

4. A process as claimed in any one of claims 1 to 3, wherein the organic base in the said solution serves also as a structure-directing agent (template) in the synthesis of the molecular sieve.

5. A process as claimed in claim 4, wherein the template is tetraethylammonium hydroxide (TEAOH).

6. A process as claimed in claim 4 or claim 5, wherein the template is a mixture of tetraethylammonium hydroxide (TEAOH) and dipropylamine (DPA).

7. A process as claimed in any one of claims 1 to 6, wherein at least part of the process is carried out with agitation of the synthesis mixture.

8. A process as claimed in any one of claims 1 to 7, wherein the silicoaluminophosphate crystalline molecular sieve is SAPO-34.

9. A process as claimed in any one of claims 1 to 8, wherein the source of silicon comprises an inorganic silicon compound.

10. A process as claimed in claim 9, wherein the inorganic silicon compound is colloidal silica.

11. A crystalline silicoaluminophosphate molecular sieve whenever produced by a process as claimed in any one of claims 1 to 10.

12. A crystalline silicoaluminophosphate molecular sieve, the mean particle size of which is at most 400 nm.

13. A process for manufacturing a crystalline molecular sieve, comprising (i) forming a synthesis mixture from a cryatlline silicoaluminophosphate molecular sieve as claimed

in claim 11 or claim 12, sources of aluminium and of silicon, optionally a source of phosphorus and optionally one or several structure-directing agents (templates) and any other material necessary to form the molecular sieve, and (ii) treating the synthesis mixture for a period and at a temperature appropriate for the manufacture of the crystalline molecular sieve.

14. The use, in the manufacture of a crystalline molecular sieve by hydrothermal treatment of a synthesis mixture containing sources of silicon and of aluminium, and optionally of phosphorus, of providing a crystalline silicoaluminophosphate molecular sieve as claimed in claim 11 or in claim 12 as seed to help forming the crystalline molecular sieve.

15. The use as claimed in claim 14, wherein the crystalline silicoaluminophosphate molecular sieve used as seed is SAPO-34.

16. The use as claimed in claim 15, wherein the particle size of SAPO-34 is such that at least 50% of the crystals are smaller than 50 nm.

17. The use, in the manufacture of a crystalline silicoaluminophosphate molecular sieve by hydrothermal treatment of a synthesis mixture containing sources of silicon, of phosphorus and of aluminium, of providing the silicon source in

the form of a solution to control the particle size of the product.

18. The use as claimed in claim 17, wherein the said solution is a basic organic solution.

19. A process for the conversion of an oxygenate to olefins which comprises contacting the oxygenate under catalytic conversion conditions with a molecular sieve as claimed in claim 11 or claim 12.

20. The use of the molecular sieve as claimed in claim 11 or claim 12, if desired after washing, cation exchange, or calcining, in hydrocarbon conersion, adsorption or separation.

21. The use of the molecular sieve as claimed in claim 11 or claim 12, if desired after washing, cation exchange, or calcining, in converting an oxygenate to olefins.

INTERNATIONAL SEARCH REPORT

Internal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01B B01J C07C

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

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

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 898 722 A (DEROUANE ERIC G ET AL) 6 February 1990 (1990-02-06) cited in the application claims 1-7 column 1, line 26-68 column 3, line 55-62 column 4, line 3-9,37-49	1-4,7,9, 11,17,18
Y	example 1 ---	5,6,8
X	WO 00 06493 A (JANSSEN MARCEL J G ;MERTENS MACHTELD M (BE); MORTIER WILFRIED J (B) 10 February 2000 (2000-02-10) cited in the application claims 1-4,8-16,19,22,23 page 2, line 4-19 page 8, line 9-25	11, 13-15, 19-21
A	examples 2-8,10,11 --- -/--	1-10,12, 16-18

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
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Internat Application No
PCT/US 02/26208

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DAHL IVAR M ET AL: "Effect of crystallite size on the activity and selectivity of the reaction of ethanol and 2-propanol over SAPO-34" MICROPOROUS AND MESOPOROUS MATERIALS, ELSEVIER SCIENCE PUBLISHING, NEW YORK, US, vol. 29, no. 1, 1999, pages 159-171, XP002160836 ISSN: 1387-1811	12
A	Page 160-161 "Synthesis" and "Fractionation", page 162-163 "Sample preparation and characteristics".	1-11, 13-21

Y	US 4 440 871 A (MESSINA CELESTE A ET AL) 3 April 1984 (1984-04-03) cited in the application claims 1,8	5,6,8
A	examples 32-38	1-4,7, 9-21

A	WO 01 36328 A (EXXON CHEMICAL PATENTS INC) 25 May 2001 (2001-05-25) cited in the application claims 1,2,10,11,13 page 2, line 27 -page 3, line 13 page 8, line 1-9 page 9, line 21-25 page 11, line 6,7 examples	1-16

INTERNATIONAL SEARCH REPORT

Inte ional application No.
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-21

1.1. Claims: 1-11,13-16, 19-21
A process for the manufacture of a crystalline molecular sieve, in which the silicon source is added to the synthesis mixture in solution with an organic base.

1.2. Claims: 12, 13-16, 19-21
A crystalline SAPO sieve, with a mean particle size of at most 400 nm.

1.3. Claims: 17, 18
The provision of a silicon source in the form of a solution during the manufacture of a crystalline molecular sieve.

Please note that all inventions mentioned under item 1, although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat Application No
PCT/US 02/26208

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