

**EXCHANGED ZEOLITES X, IN PARTICULAR EXCHANGED WITH LITHIUM,
THEIR PROCESS OF PREPARATION AND THEIR USE AS ADSORBENTS OF
NITROGEN IN THE SEPARATION OF THE GASES OF THE AIR**

The invention relates to X type zeolites, their preparation and their use in the separation of gas mixtures. More particularly the invention relates to X type zeolites exchanged with lithium and with trivalent and/or divalent ions which are selective for nitrogen and which have improved thermal stability and crystallinity, their preparation
5 and their use in the separation of nitrogen from less strongly adsorbed gases.

The separation of nitrogen from other gases, such as, for example, oxygen, argon and hydrogen, is of considerable industrial importance. When the separation is carried out on a large scale, fractional distillation is often used. However, distillation is very expensive because of the high initial cost of the plant and the considerable energy
10 demand which it involves. Other separation methods have recently been studied in efforts to reduce the overall cost of separation.

An alternative to distillation which has thus been used to separate nitrogen from other gases is adsorption. For example, the sodium zeolite X disclosed in US patent specification US 2 882 244 has been used for the separation by adsorption of nitrogen
15 from oxygen. One disadvantage of the use of sodium zeolite X for the separation of nitrogen from oxygen is that it only has a low separating efficiency in the separation of nitrogen.

According to US patent specification US 3 140 933, an improvement in the adsorption of nitrogen is obtained when some of the base ions are replaced by lithium
20 ions. This patent specification states that X type zeolites having base ions replaced by lithium ions can be efficiently used to separate nitrogen from oxygen at temperatures ranging up to 30°C. As the exchange of ions is not total, and the zeolites X have been synthesised in a sodium medium, the adsorbent used is a mixed sodium/lithium zeolite.

US patent specification US 4 859 217 teaches that very good separation of
25 nitrogen from oxygen can be obtained by adsorption at temperatures of 15 to 70°C using an X type zeolite which has more than 88% of its ions in the form of lithium ions, in particular when a zeolite is used with a silicon/aluminium atomic ratio of between 1 and 1.25.

Unfortunately, X type zeolites highly exchanged with lithium have a very

strong affinity for water and the presence of adsorbed water, even small amounts, seriously reduces the adsorption capacity of the zeolites. Consequently, in order to ensure optimum performance as regards adsorption, it is necessary to activate the zeolites by heating to temperatures ranging up to 600 to 700°C in order to drive off as much adsorbed water as possible. However, X type zeolites exchanged with lithium are not stable at temperatures greater than approximately 740°C. Accordingly, activation of these adsorbents must be carefully controlled in order to prevent them from being damaged. Another disadvantage of X type zeolites highly exchanged with lithium is that they have a high production cost due to the price of the lithium compounds needed in their manufacture.

A need thus exists for adsorbents which have good thermal stability, good crystallinity and adsorbent properties for nitrogen at least equal to those of zeolites highly exchanged with lithium but which can be produced at a more reasonable cost.

US patent specification US 5 179 979 teaches that lithium/alkaline earth metal X type zeolites having lithium/alkaline earth metal molar ratios of the order of approximately 95/5 to 50/50 have a higher thermal stability than that of the corresponding zeolites with pure lithium and good adsorption selectivities and capacities.

US patent specification US 5 152 813 discloses the adsorption of nitrogen from gas mixtures using crystalline zeolites X having an Si/Al zeolite ratio ≤ 1.5 in which the exchangeable sites are occupied by at least 2 ions: between 5 and 95% of lithium ion and between 5 and 95% of a second ion chosen from calcium, strontium and mixtures thereof, the total (lithium and second exchangeable ion) being at least 60%.

US patent specification US 5 464 467 and European patent specification EP 667 183 describe an X type zeolite, the cations of which comprise, referred to as equivalents, from approximately 50 to approximately 95% of lithium, from approximately 4 to approximately 50% of trivalent ions chosen from aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide, mixtures of two or more lanthanides, and mixtures thereof, and from 0 to approximately 15% of

residual ions chosen from sodium, potassium, ammonium, hydronium, calcium, strontium, magnesium, barium, zinc, copper(II) and mixtures thereof, which is prepared by exchange of the exchangeable cations of the zeolite, preagglomerated with a binder, first with lithium and then with the trivalent cation or cations.

5 US patent specification US 5 932 509 describes the preparation of the same zeolites according to a process which consists of exchanging the exchangeable cations of the powdered zeolite X with trivalent cations, then agglomerating with a binder and finally carrying out the lithium exchange on the agglomerated zeolite.

10 However, it has now been found that although the zeolites prepared according to US patent specifications US 5 179 979, US 5 152 813, US 5 464 467 and US 5 932 509 exhibit good thermal stability and a good nitrogen adsorption capacity, they have insufficient crystallinity and exhibit a degree of heterogeneity in the distribution of the tri- and/or divalent cations.

The subject of the present invention is X type zeolites having an Si/Al
15 atomic ratio of less than 1.5, preferably between 0.9 and 1.1, the exchangeable cations of which comprise, referred to as equivalents,

- from approximately 50 to approximately 95% of lithium ions,
- from approximately 4 to approximately 50% of trivalent ions chosen from aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanides or
20 rare earth metals, alone or as a mixture, and/or of divalent ions chosen from calcium, strontium, zinc, copper, chromium(II), iron(II), manganese, nickel or cobalt, alone or as a mixture, and

- 0 to approximately 15% of residual ions chosen from sodium, potassium, ammonium or hydronium, alone or as a mixture,

25 which are capable of being obtained according to a process which comprises the following stages:

- a) suspension of the zeolite in water, then
- b) exchange of the exchangeable cations of the suspended zeolite with one or more di- and/or trivalent ions by simultaneous and/or successive contact(s) in a rapid

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mixer of the said suspension with one or more solutions comprising compounds of the di- and/or trivalent ions,

c) exchange of the exchangeable cations of the zeolite resulting from stage b) with lithium,

5 which stages will be explained in detail below.

According to one aspect of the present invention there is provided a process for the preparation of an X type zeolite having an Si/Al atomic ratio of less than 1.5, the exchangeable cations of which comprise, referred to as equivalents,

- from approximately 50 to approximately 95% of lithium ions,
10 - from approximately 4 to approximately 50% of trivalent aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide or rare earth metal ions, or a mixture thereof, and/or of divalent calcium, strontium, zinc, copper, chromium(II), iron(II), manganese, nickel or cobalt ions, or a mixture thereof, and

15 - 0 to approximately 15% of sodium, potassium, ammonium or hydronium ions, or a mixture thereof, which process comprises

a) suspending the zeolite in water,

b) exchanging the exchangeable cations of the suspended zeolite with one or more di- and/or trivalent ions by simultaneously and/or successively

20 contacting in a rapid mixer, the suspension with one or more solutions comprising compounds of the di- and/or trivalent ions, and

c) exchanging the exchangeable cations of the zeolite resulting from stage b) with lithium.

According to another aspect of the present invention there is provided
25 an X type zeolite having an Si/Al atomic ratio of less than 1.5, the exchangeable cations of which comprise, referred to as equivalents,

- from approximately 50 to approximately 95% of lithium ions,

- from approximately 4 to approximately 50% of trivalent aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide or rare earth
30 metal ions, or a mixture thereof, and/or of divalent calcium, strontium, zinc, copper,

chromium(II), iron(II), manganese, nickel or cobalt ions, or a mixture thereof, and
- 0 to approximately 15% of sodium, potassium, ammonium or hydronium
ions, or a mixture thereof,
capable of being obtained by the process described above.

5 The zeolites of the present invention can be provided in various forms and
the exact form which they assume can determine their usefulness in industrial adsorption
processes. When the zeolites of the present invention are used in industrial adsorbers, it
may be preferable to agglomerate (for example, to convert into granules) the zeolite in
order to avoid compacting the pulverulent zeolite in an adsorption column of industrial
10 size, thus blocking or greatly reducing the flow through the column. These techniques
generally involve mixing the zeolite with a binder, which is usually a clay, converting
the mixture to an agglomerate, for example by extrusion or bead formation, and heating
the zeolite/binder mixture formed to a temperature of approximately 600-700°C in order
to convert the "green" agglomerate to an agglomerate which is resistant to crushing. The
15 binders used to agglomerate the zeolites are generally inorganic and inert with respect to
adsorption. Binders suitable for use according to the invention include clays, silicas,
aluminas, metal oxides or their mixtures.

It is possible to prepare agglomerates comprising less than 10 %, for
example less than 5%, by weight of residual binder. A process for producing these
20 agglomerates with a low level of binder comprises converting the binder of the
agglomerates described above to the zeolite phase. This process comprises
agglomerating a zeolite LSX powder with a binder which can be converted to zeolite (for
example kaolin or metakaolin), converting the binder to zeolite by alkaline maceration,
for example according to the process disclosed in European patent specification
25 EP 932 581, and then exchanging the granule which has been converted to zeolite with
sodium. It is thus possible to easily obtain according to the invention outstandingly
effective agglomerates assaying at least 90 %, indeed even at least 95%, of zeolite LSX.

In addition, the zeolites can be agglomerated with materials such as
silica/alumina, silica/magnesia, silica/zirconia, silica/thoria, silica/beryllium oxide and

silica/titanium dioxide, as well as with ternary compositions, such as silica/alumina/thoria, silica/alumina/zirconia and clays present as binders. The relative proportions of the materials and of the zeolites mentioned above can vary widely. When the zeolite has been converted to agglomerates before use, these agglomerates
5 advantageously have a diameter of approximately 0.5 to approximately 5 mm.

The agglomeration binder generally represents from 5 to 30 parts by weight per 100 parts of agglomerate.

The zeolites according to the invention have an improved thermal stability and crystallinity with respect to zeolites of the prior art with the same degree of
10 exchange of lithium and of di- and/or trivalent cations. They are particularly effective as adsorbents of the nitrogen present in various gas mixtures and are well suited to the noncryogenic separation of the gases of the air.

The zeolites of the invention are generally prepared from a base X type zeolite which usually originally has sodium and/or potassium ions as charge-
15 compensating cations. By "charge-compensating cations" as used herein is meant ions which compensate for the negative charge of the aluminosilicate lattice.

The exchangeable cations of the starting zeolite are typically exchanged with a solution of the compounds of the trivalent ions and/or of the divalent ions (stage b)) by simultaneously pumping the suspension of zeolite to be exchanged, suspended
20 beforehand in water (stage a)), and the solution of the compounds by forcing them to pass through a rapid mixer capable of providing homogeneous mixing of the suspension and of the solution after a short time of contact between the suspension and the solution (a few minutes), which mixer is preferably a static mixer capable of providing homogeneous mixing after a very short contact time (a few seconds), all arrangements
25 being made in order for the flow rates to be adjusted so as to retain a weight of suspension/weight of solution ratio which is virtually constant. Recourse to exchange in a static mixture has no effect with regard to the degree of exchange, which remains the quantitative degree achieved by conventional exchange. A better random distribution of

the di- and/or trivalent ions within the zeolite structure is obtained, which is reflected by a final level for the nitrogen adsorption capacity which is significantly improved, which is entirely unexpected.

It is preferable, but not essential, to use aqueous solutions of the exchange
5 ions. Any water-soluble compound of the exchanging ions can be used. Preferred water-soluble compounds of the ions suitable for use according to the invention are the salts and in particular the chlorides, sulfates and nitrates. The particularly preferred salts are the chlorides, because of their high solubilities and their ready availability.

The zeolites according to the invention, in which a portion of the cationic
10 sites are occupied by several types of divalent and/or trivalent ions as defined above, can be prepared either by simultaneously exchanging all the cations, by contact with a solution comprising all the cations, or by carrying out a successive exchange of each cation, or by using a solution intermediate between the two above solutions.

A preferred embodiment of the invention comprises exchanging the
15 exchangeable cation or cations with tri- and/or divalent ions and with monovalent ions, preferably the sodium ion.

In one embodiment the exchangeable cations of the zeolite resulting from
stage a) and/or from stage b) can be exchanged with a monovalent cation, for example an ammonium or sodium ion. In addition, the cationic exchange of stage b) can be carried
20 out in the presence of one or more compounds of a monovalent ion such as an ammonium or sodium ion.

Another preferred embodiment comprises stabilizing, with sodium
hydroxide, the zeolite immediately after the exchange with tri- and/or divalent ions or after the exchange with tri- and/or divalent ions and monovalent ions.

25 When the zeolites according to the invention are provided in agglomerated form, a particularly preferred form, the agglomerated stage is carried out after the exchange of a portion of the exchangeable cations of the zeolite with tri- and/or divalent cations, optionally in the presence of a monovalent cation.

It is particularly advantageous to convert all the exchangeable cations of the

starting zeolite to a single monovalent cationic species, preferably the sodium or ammonium ion form, prior to the exchange with the di- and/or trivalent cations as explained above. For this, the zeolite is brought into contact with a solution comprising monovalent ions, such as sodium or ammonium, for example an aqueous NaCl or NH₄Cl solution.

Once exchanged with di- and/or trivalent ions, the zeolite can also be advantageously brought into contact, before or after the optional agglomeration stage, with a solution comprising sodium or ammonium ions, for example an aqueous NaCl or NH₄Cl solution.

Stage c) of the process according to the invention comprises exchanging a portion of the exchangeable cations with lithium ions by contact with a lithium compound solution, preferably an aqueous solution of lithium salt, such as LiCl. After each ion exchange stage the zeolite is generally washed with water and then dried at a temperature generally of between 40 and 200°C by methods known in the art.

Preferably, at atmospheric pressure, the temperature of the solution of lithium compounds is between 80 and 115°C and in particular between 95 and 115°C. Higher temperatures can be used, with pressurization of the system.

The concentration of lithium in the solution is limited by the solubility of the salts and is generally chosen to be as high as possible in order to reduce the cost related to reprocessing.

A particularly advantageous embodiment comprises carrying out the operation countercurrent-wise and continuously according to the procedure described in European patent specification EP 863 109 as described below.

The zeolite is distributed in at least 2, preferably at least 3, receptacles in the stationary bed form which are arranged in series in an interchangeable manner, the solution of lithium compounds is conveyed through the said receptacles arranged in series and the sequence of the receptacles arranged in series, known as a "carousel", is modified cyclically at given time intervals, the inlet of the fresh solution being moved on each occasion from the 1st receptacle, in which is found the zeolite which has been

exchanged with lithium to the greatest extent, to the following receptacle in the series; when the desired degree of exchange of lithium is reached for the zeolite in the 1st receptacle, the latter is taken out of the series of receptacles of the carousel and the zeolite which is present therein is freed from the solution of lithium compounds by washing, then discharged and optionally replaced by a fresh charge of zeolite to be exchanged.

The cycle time of a time interval is typically at least 15 minutes and preferably at least 1 hour.

According to a further aspect of the present invention there is provided use of the zeolites according to the invention as adsorbents of nitrogen present in a gas mixture and in particular air, thus making it possible to separate the nitrogen from the other gases present in the gas mixture. The separation is carried out by passing the gas mixture into at least one adsorption region comprising an adsorbent composed essentially of a zeolite as defined in the invention.

In a preferred embodiment, the adsorption process is cyclic and comprises the adsorption stage described above and a stage of desorption of the nitrogen from the adsorption region(s).

The preferred cyclic processes encompass adsorption by pressure variation (PSA for Pressure Swing Adsorption or VSA for Vacuum Swing Adsorption (specific case of desorption under vacuum)), by temperature variation (TSA for Temperature Swing Adsorption) and combinations of these (PTSA).

According to some preferred embodiments, the adsorption stage is carried out at a temperature of between approximately -20 and approximately 50°C and at an absolute pressure of between approximately 0.08 and 1 MPa.

In a highly preferred embodiment of the invention, the adsorption process is used to separate the nitrogen from a gas mixture comprising nitrogen and one or more other gases chosen from oxygen, argon, helium, neon and hydrogen.

In other preferred embodiments of the invention, the adsorption zone is regenerated by vacuum means (suction), by purging the adsorption zone with one or

more inert gas(es) and/or with a part of the gas mixture coming out the adsorption zone, by temperature variation or by combination of these regenerations by suction, by purging and/or temperature variation. In general, the repressurization of the bed is at least partially carried out by using the nonadsorbed gas from the adsorption system.

- 5 The temperature at which the adsorption stage of the adsorption process is carried out depends on a number of factors, such as the specific gases to be separated, the specific adsorbent used and the pressure at which the adsorption is carried out. In general, the adsorption stage is carried out at a temperature of at least approximately 20°C and advantageously at a temperature of at least approximately 15°C. The
- 10 adsorption is generally carried out at temperatures which are not greater than approximately 70°C, preferably at temperatures which are not greater than 50°C and more preferably at temperatures which do not exceed approximately 35°C.

- The adsorption stage of the adsorption process according to the invention can be carried out at any of the usual and well known pressures used in adsorption
- 15 processes of TSA, PSA or VSA type. Typically, the minimum absolute pressure at which the adsorption stage is carried out is generally at least equal to atmospheric pressure. The maximum absolute pressure at which the adsorption stage is carried out generally does not exceed approximately 1.5 MP, preferably approximately 1 MPa and advantageously approximately 0.4 MPa.

- 20 When the adsorption process is adsorption by pressure variation, the adsorbent is generally regenerated at a pressure of between 10 and 500 kPa, preferably from 20 to 200 kPa approximately, lower than the adsorption pressure and, when it is adsorption by temperature variation, it is generally regenerated at a temperature of between 0 and 300°C approximately, greater than the adsorption temperature.

- 25 When the adsorption process is of TSA type, the temperature of the bed(s) is increased during the regeneration stage with respect to the adsorption temperature. The regeneration temperature can be any temperature below that at which the adsorbent begins to decompose. Generally, the temperature of the adsorbent is usually increased to a value of between approximately 0 and approximately 300°C, preferably between

approximately 25 and 250°C and advantageously between approximately 50 and 180°C. The regeneration procedure can be a combination of PSA or VSA and of TSA, in which case both the temperature and the pressure used during the regeneration will vary within the ranges indicated above.

5 The Examples which follow illustrate the invention.

Example 1 (comparative according to European patent specification EP 667 183 (BOC))

1 000 litres of softened industrial water are introduced into a vessel equipped with a propeller stirrer. 200 kg of powdered zeolite LSX (amount considered as
10 anhydrous product), with an Si/Al atomic ratio equal to 1, the exchangeable cationic sites of which are 77% occupied by sodium and 23% occupied by potassium, with a micropore volume equal to 0.262 cm³/g (measured by toluene adsorption at 25°C under a relative pressure of 0.5) and with a Dubinin volume equal to 0.325 cm³/g, are added with stirring (100 rev/min and peripheral speed = 3.5 m/s). 45 kg of solution of industrial
15 rare earth metal chlorides, which solution is sold by Rhodia under the name LADI (aqueous solution comprising lanthanum and praseodymium chlorides at concentrations, expressed as La₂O₃ and Pr₂O₃, of 16.6 and 7.2% by weight respectively, the remainder being predominantly composed of water and of traces of chlorides of other rare earth metals (Ce, Nd)), are subsequently introduced over approximately 10 minutes. The
20 stirring is decreased to 20 rev/min and the reactor is maintained under these conditions for approximately 1 hour, at the end of which time it is found that the mixture is finally homogeneous, after which the powder thus obtained is filtered off, washed and dried.

The powder is subsequently agglomerated using a clayey binder at the level of 17% by weight (considered with respect to the agglomerate). The product is shaped in
25 the form of beads with a diameter of 1.6-2.5 mm. These beads are dried at 80°C and then activated according to the LTC (traversed bed) technology, for example disclosed in European patent specification EP 421 875, at 580°C under dry air devoid of carbon dioxide.

Exchange with lithium is then carried out, which consists of subjecting the

above beads to the action of a 4M aqueous lithium chloride solution at 110°C, the solution/mass of the beads ratio by volume being 10. This exchange is carried out 6 times, which ensures the virtually complete removal of the sodium and potassium ions initially present in the structure of the zeolite LSX. The resulting product is dried at
 5 60°C and then activated according to the LTC technology at a temperature of 580°C under dry air devoid of carbon dioxide.

The analysis of the ions of the product, expressed as percentage of the initial zeolite LSX exchange capacity, is thus:

	rare earth metal equivalents	14%
10	sodium + potassium equivalents	1%
	lithium equivalents	85%

Example 2

1 000 litres of softened industrial water are introduced into a vessel equipped with a propeller stirrer. 200 kg of powdered zeolite LSX, the characteristics of which are
 15 shown in Example 1, are added with stirring (100 rev/min and peripheral speed = 3.5 m/s). 45 kg of LADI solution of industrial rare earth metal chlorides are measured into a second vessel.

The suspension of zeolite LSX and the solution of rare earth metal chlorides are then simultaneously pumped while forcing them to pass through the same static
 20 mixer. The flow rates are adjusted so as to continually retain a weight of suspension/weight of solution ratio equal to 1 200/45. The mixture exiting from the static mixer is stored in a third vessel with gentle stirring for one hour, after which the solid is filtered off, washed and dried.

This solid is subjected to the same agglomeration, intermediate activation,
 25 lithium exchange and final activation actions as in Example 1. The analysis of the ions in the exchanged structure leads to the same results as in Example 1.

Example 3

The adsorbents based on rare earth metal/lithium zeolite prepared in

Examples 1 and 2 are tested with regard to their nitrogen adsorption capacities (C_{N_2}) at 25°C and under a pressure of 100 kPa, after conditioning by degassing under a vacuum of 10^{-3} mm of mercury at 300°C for 3 hours. The Dubinin volume of these adsorbents is also measured.

5 The following results are obtained:

Type of adsorbent	C_{N_2} at 100 kPa at 25°C (cm ³ /g)	Dubinin volume
According to Example 1 (comparative)	20.5	0.28
10 According to Example 2	21.2	0.29

It is deduced from these results that the adsorbent according to the invention prepared in Example 2 has a better nitrogen adsorption potential than the adsorbent prepared in Example 1 according to the teaching of European patent specification EP
15 667 183 as it exhibits a more homogeneous distribution of the load of rare earth metals which is reflected in the adsorption properties of the final product.

The following Examples 4 to 7 were carried out on the laboratory scale by introducing the solution of rare earth metal chlorides dropwise into the zeolite suspension: this corresponds to an immediate dispersion as obtained on the industrial
20 scale with a static mixer.

Example 4

20 g of powdered zeolite LSX as defined in Example 1 are introduced into 200 g of water with stirring. After homogenizing the suspension, 34.5 g of solution of rare earth
25 metal chlorides diluted in water, composed of 30 ml of water and of 4.5 g of LADI solution of rare earth metal chlorides, are added dropwise over 20 minutes. After complete addition, stirring is halted and the reaction mixture is maintained at room temperature for 2 hours, then filtration is carried out and the cake thus obtained is washed and dried at room temperature; this method is known as route 1.

According to a second method, known as route 2, the 30 ml of water of the solution of rare earth metal chlorides diluted in the above water are replaced with 30 ml of a 2M aqueous NaCl solution, which results in an overall concentration of Na in the reaction mixture of the order of 0.35M. A competitive exchange is carried out here
 5 between the rare earth metal cations and the sodium cations present.

The zeolite powders obtained by routes 1 and 2 are chemically analysed, both by conventional chemical analysis and by XPS spectroscopy (X-ray photoelectron spectroscopy), which allows the surface of the sample to be affected only over a thickness of the order of a few tens of Å; it is thus possible to ascertain whether the
 10 surface is similar to the overall composition.

The results are as follows:

		Route 1	Route 2
15 Overall chemical analysis	Degree of rare earth metal exchange (%)	14.8	13.2
	Degree of Na exchange (%)	58.6	68.6
	Degree of K exchange (%)	19.8	14.9
	Cationic compensation (%)	93	97
20 Chemical analysis by XPS	Degree of rare earth metal exchange (%)	86	59

The inventors believe that the 100% cationic closure is provided by protons; this would imply that route 1 provides a product which is slightly more acidic than that of route 2.

In the light of these results, it is concluded that the competitive exchange
 25 with NaCl (route 2) makes it possible:

- to improve the homogeneity in distribution of the ions in the zeolite
- to reduce the residual potassium content
- to improve the cationic compensation.

The inventors believe that all these elements militate in favour of an
 30 improvement in the quality of the powder for the purpose of subsequent shaping and subsequent exchange.

Example 5

20 grams (considered as anhydrous equivalents) of powdered LSX as defined in Example 1 are dispersed in 118 ml of water with gentle stirring. 115 ml of an aqueous solution also comprising 5 g of LADI solution of rare earth metal chlorides and 37 g of NaCl are added to this suspension, which results in an overall concentration of sodium of 2.7M. A competitive exchange is thus carried out here between the rare earth metals and the sodium. After complete addition of the solution, stirring is halted and the reaction mixture is maintained at room temperature for 2 hours, then filtration is carried out and the cake thus obtained is washed and dried at room temperature.

The zeolite powder obtained is chemically analysed, both by conventional chemical analysis and by XPS spectroscopy; the results are as follows:

Overall chemical analysis	Degree of rare earth metal exchange (%)	16
	Degree of K exchange (%)	4.5
	Degree of Na exchange (%)	79.5
	Cationic compensation (%)	100
Chemical analysis by XPS	Degree of rare earth metal exchange (%)	47.5

These values thus clearly show, just like those in Example 4, that success is achieved in providing a better distribution of the rare earth metals by the rare earth metals/sodium competitive exchange. At the same time, the cationic compensation shows that no protons are retained. Finally, the degree of exchange of potassium decreases to low levels.

This powder is subsequently agglomerated using the same clay binder as that in Example 1, the powder being shaped into the form of beads with a diameter of 1.6 to 2.5 mm. These beads are dried at 80°C and then activated according to the LTC technology at 580°C. The lithium exchange, which consists in subjecting the beads to the same treatment as that described in Example 1, is subsequently carried out. The resulting product is dried at 60°C and then activated according to the LTC technology at

580°C under dry air devoid of carbon dioxide.

The analysis of the ions in the product, expressed as a percentage of the initial zeolite LSX exchange capacity, is thus:

	rare earth metal equivalent	16%
5	sodium and potassium equivalent	1%
	lithium equivalent	83%

The adsorbent in question is tested with regard to its nitrogen adsorption capacity at 25°C and under a pressure of 100 kPa, after degassing at 300°C under a vacuum of 0.13 Pa for 3 hours. The following results are obtained:

10	C_{N_2} at 100 kPa at 25°C	22.1 cm ³ /g
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The Dubinin volume is measured by making use of the N₂ adsorption isotherm at 77°K, measured on the degassed samples; a Dubinin volume of 0.290 cm³/g is obtained.

These results thus clearly confirm that the adsorbents prepared according to the preferred process of the invention (competitive di- or trivalent cation/monovalent cation exchange) exhibit a greater nitrogen adsorption capacity than that of those for which the rare earth metal exchange did not take place in the presence of sodium ion.

Example 6

20 An exchange of a portion of the exchangeable Na⁺ and K⁺ cations of the zeolite LSX defined in Example 1 with rare earth metal cations is carried out by mixing a suspension of 10 g of zeolite and of 70 g of water with 2.33 g of a LADI solution of rare earth metal chlorides at room temperature for 2 hours, in order to achieve a degree of exchange of 15% according to the process described in Example 1. After 1 h 45 of
25 contact between the aqueous zeolite suspension and the rare earth metal chloride solution, a small amount of sodium hydroxide (in a proportion of 0 g, 0.6 g and 2 g respectively of sodium hydroxide per kg of exchanged zeolite powder) is added to the reaction medium in order to compensate for the protons and the mixture is kept stirred for 15 minutes. The suspension is filtered and the zeolite is washed with approximately

15 ml of water per gram of zeolite. Chemical analysis of the powder not stabilized with sodium hydroxide at the end of the exchange shows that approximately 7% of the cationic sites are occupied by protons, which is not surprising in so far as the exchange was carried out using a slightly acidic solution.

- 5 A few grams of exchanged and optionally stabilized zeolite powder are subsequently dried in a ventilated oven for 1 h at 80°C and then activated at 550°C for 1 hour in the same type of ventilated oven. Their micropore volume is subsequently measured by absorption of toluene under a relative pressure of 0.5 at 25°C. The results are combined in the table below:

10

Amount of sodium hydroxide added per kg of exchanged zeolite	0 g	0.6 g	2 g
Micropore volume (cm ³ /g)	0.228	0.237	0.25

- 15 It is seen that the stabilization with sodium hydroxide results in a greater micropore volume and confers better thermal resistance (better resistance to calcination) on the zeolite.

Example 7

- 20 An exchange of a portion of the exchangeable Na⁺ and K⁺ cations of the zeolite LSX defined in Example 1 with Zn²⁺ cations is carried out by mixing 1 200 g of an aqueous suspension comprising 200 g of zeolite with 90 ml of an aqueous ZnCl₂ solution, the zinc concentration of which is 0.1M, at 80°C for 3 hours; the pH of the reaction mixture being equal to 7.

- 25 In an alternative form of the process, stabilization with sodium hydroxide is carried out at the end of exchange by addition of a concentrated sodium hydroxide solution in a proportion of 22.5 g of sodium hydroxide added per kg of Zn-exchanged zeolite.

- 30 The subsequent washing, drying and activation operations are carried out under similar conditions to those described in the preceding examples. The micropore

volume and the percentage of the cationic sites occupied by protons are then measured; the results are combined in the table below:

5	Amount of sodium hydroxide added per kg of exchanged zeolite (g)	22.5	0
	Degree of exchange of zinc (%)	14	13.7
	Micropore volume (cm ³ /g)	0.260	0.262
	Percentage of the cationic sites occupied by protons	2	5

10 It is found that the stabilization treatment with sodium hydroxide had the effect of

- decreasing the number of protons in the solid but the micropore volumes measured are substantially identical

- slightly improving the efficiency of exchange of zinc, which changes
15 from 98% to virtually 100%, which is particularly advantageous in so far as less zinc is discharged.

The powdered zeolite, exchanged with zinc and optionally stabilized with sodium hydroxide, is subsequently agglomerated with a binder (17% of binder in the agglomerate) and then exchanged with lithium under the same conditions as in the
20 preceding examples: bringing into contact at 100°C of 3.6 g of agglomerated zeolite exchanged with zinc, optionally stabilized with sodium hydroxide, prepared above and 30 ml of a 4M aqueous LiCl solution; after contact, the agglomerates are filtered, washed and dried. It is found that the degree of exchange of zinc of the zeolite which has not been stabilized with sodium hydroxide fell to 8% after the lithium exchange, which
25 means that a good part of the zinc has been released (back exchange) during the exchange with lithium. The release in question is estimated at 1.3 g of zinc per litre of solution at equilibrium.

Unexpectedly, the degree of exchange of zinc of the zeolite which has been stabilized with sodium hydroxide does not vary after the lithium exchange and, in fact, it
30 is found that, at equilibrium, the content of zinc in the aqueous liquors after lithium

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exchange is very much less than 50 ppm, a sign that release is insignificant.

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CLAIMS

1. Process for the preparation of an X type zeolite having an Si/Al atomic ratio of less than 1.5, the exchangeable cations of which comprise, referred to
5 as equivalents,
- from approximately 50 to approximately 95% of lithium ions,
 - from approximately 4 to approximately 50% of trivalent aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide or rare earth metal ions, or a mixture thereof, and/or of divalent calcium, strontium,
10 zinc, copper, chromium(II), iron(II), manganese, nickel or cobalt ions, or a mixture thereof, and
 - 0 to approximately 15% of sodium, potassium, ammonium or hydronium ions, or a mixture thereof, which process comprises
- a) suspending the zeolite in water,
 - 15 b) exchanging the exchangeable cations of the suspended zeolite with one or more di- and/or trivalent ions by simultaneously and/or successively contacting in a rapid mixer, the suspension with one or more solutions comprising compounds of the di- and/or trivalent ions, and
 - c) exchanging the exchangeable cations of the zeolite resulting from
20 stage b) with lithium.
2. Process according to Claim 1, wherein the Si/Al atomic ratio of the X type zeolite is between 0.9 and 1.1.
- 25 3. Process according to Claim 1 or 2, wherein stage b) is carried out in a static mixer.
4. Process according to any one of the preceding Claims, which further comprises agglomerating the zeolite resulting from stage b) with a binder.
- 30 5. Process according to any one of the preceding Claims, which further

comprises exchanging the exchangeable cations of the zeolite resulting from stage a) and/or from stage b) with a monovalent cation.

6. Process according to Claim 5, wherein the monovalent cation is an ammonium or sodium ion.

7. Process according to any one of the preceding Claims, wherein the cationic exchange of stage b) is carried out in the presence of one or more compounds of a monovalent ion.

8. Process according to Claim 7, wherein the monovalent ion is an ammonium or sodium ion.

9. Process according to any one of the preceding Claims, which further comprises stabilizing with sodium hydroxide immediately after the exchange with tri- and/or divalent ions or with tri- and/or divalent ions and monovalent ions of stage b).

10. Process according to any one of the preceding Claims, wherein the lithium exchange (stage c)) is carried out countercurrentwise and continuously, the zeolite being distributed in at least 2 receptacles in the stationary bed form which are arranged in series in an interchangeable manner, the solution of lithium compounds being conveyed through the said receptacles arranged in series and the sequence of the receptacles arranged in series, known as a "carousel", being modified cyclically at given time intervals, the inlet of the fresh solution being moved on each occasion from the 1st receptacle, in which is found the zeolite which has been exchanged with lithium to the greatest extent, to the following receptacle in the series; when the desired degree of exchange of lithium is reached for the zeolite in the 1st receptacle, the latter is taken out of the series of receptacles of the carousel and the zeolite which is present therein is freed from the solution of lithium compounds by washing, then discharged and

optionally replaced by a fresh charge of zeolite to be exchanged.

11. Process according to Claim 10, wherein the zeolite is distributed in at least 3 receptacles.

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12. Process according to Claim 1, substantially as described in any one of Examples 2 or 4 to 7.

13. An X type zeolite having an Si/Al atomic ratio of less than 1.5, the
10 exchangeable cations of which comprise, referred to as equivalents,
- from approximately 50 to approximately 95% of lithium ions,
- from approximately 4 to approximately 50% of trivalent aluminium,
scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide or rare earth
metal ions, or a mixture thereof, and/or of divalent calcium, strontium, zinc, copper,
15 chromium(II), iron(II), manganese, nickel or cobalt ions, or a mixture thereof, and
- 0 to approximately 15% of sodium, potassium, ammonium or hydronium
ions, or a mixture thereof,
capable of being obtained by the process claimed in any one of Claims 1 to

12.

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14. A zeolite according to Claim 13, wherein the Si/Al atomic ratio is between 0.9 and 1.1.

15. A zeolite according to Claim 13 or 14, wherein the zeolite is agglomerated
25 with an inorganic binder which is inert with respect to adsorption and wherein the zeolite
is capable of being obtained by the process claimed in Claim 4.

16. A zeolite according to Claim 15, wherein the binder represents from 5 to 30 parts by weight of the agglomerate.

17. A zeolite according to Claim 15 or 16, wherein the binder is a clay, silica, alumina or metal oxide, or a mixture thereof.
18. A zeolite according to Claim 13, substantially as described in any one of
5 Examples 2 or 4 to 7.
19. Use of a zeolite as defined in any one of Claims 13 to 18 in separating nitrogen from a gas mixture according to an adsorption process comprising passing the said gas mixture into at least one adsorption region comprising an adsorbent composed
10 essentially of a zeolite as defined in any one of Claims 13 to 18.
20. Use according to Claim 19, wherein the adsorption process is cyclic and comprises desorbing the nitrogen from the adsorption region.
- 15 21. Use according to Claim 20, wherein the adsorption process is of PSA, VSA and/or TSA type.

ABSTRACT**EXCHANGED ZEOLITES X, IN PARTICULAR EXCHANGED WITH
LITHIUM, THEIR PROCESS OF PREPARATION AND THEIR USE AS
ADSORBENTS OF NITROGEN IN THE SEPARATION OF
5 THE GASES OF THE AIR**

The present invention relates to zeolites X which have been exchanged with lithium and di- and/or trivalent cations.

According to the invention there is provided an X type zeolite having an Si/Al atomic ratio of less than 1.5, the exchangeable cations of which comprise, referred
10 to as equivalents,

- from approximately 50 to approximately 95% of lithium ions,
- from approximately 4 to approximately 50% of trivalent aluminium, scandium, gallium, iron(III), chromium(III), indium, yttrium, lanthanide or rare earth metal ions, or a mixture thereof, and/or of divalent calcium, strontium, zinc, copper,
15 chromium(II), iron(II), manganese, nickel or cobalt ions, or a mixture thereof, and
 - 0 to approximately 15% of sodium, potassium, ammonium or hydronium ions, or a mixture thereof, which is capable of being obtained by a process comprising
 - a) suspending the zeolite in water,
 - b) exchanging the exchangeable cations of the suspended zeolite with one or
20 more di- and/or trivalent ions by simultaneously and/or successively contacting in a mixer, the suspension with one or more solutions comprising compounds of the di- and/or trivalent ions, and
 - c) exchanging the exchangeable cations of the zeolite resulting from stage b) with lithium.

25 The zeolites according to the present invention have improved thermal stability and crystallinity with respect to zeolites of the prior art with the same degree of exchange of lithium and of di- and/or trivalent cations. They are particularly effective as adsorbents of the nitrogen present in various gas mixtures and are well suited to the noncryogenic separation of the gases of the air.