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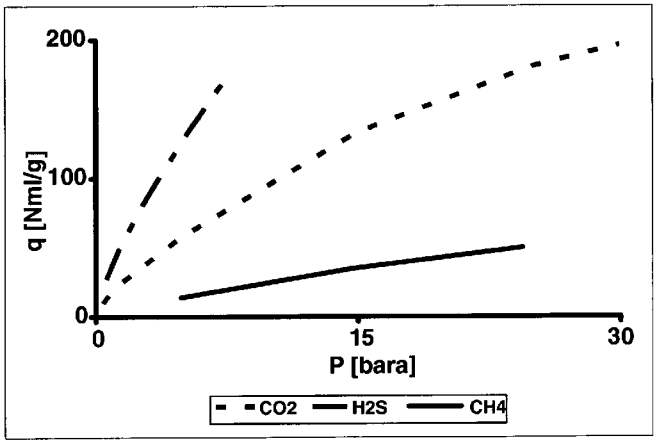
(54) **Title**: PROCESS FOR GAS SEPARATION

Fig. 1



(57) **Abstract**: The present invention relates to a process for the separation of gases which comprises putting a mixture of gases in contact with a porous material, containing a silica matrix in which one or more metal oxides are possibly uniformly dispersed, which are selected from transition metals or from metals of groups IIIA, IVA and VA, having a surface area larger than 500 m2/g, a pore volume between 0.3 and 1.3 ml/g, a pore diameter smaller than 40 Angstrom and a XRD powder spectrum which does not have a crystalline structure, does not show any peak, and has a single broad diffraction line, or, in any case, a wide¬ spread scattering at angular values not higher than $2\theta = 5°$ with CuKa radiation, without any other scattering phenomena coherent for higher angular values. By means of the process of the present invention, the selective adsorption is obtained of at least one of the gases forming the gaseous mixture. These adsorbing materials are regenerable and are particularly suitable for bulk removal operations of acid gases from natural gas.

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PROCESS FOR GAS SEPARATION

DESCRIPTION

The present invention relates to a process for the separation of gases comprising putting a mixture of gases in contact with a particular porous material, containing a silica matrix in which one or more metal oxides are possibly uniformly dispersed, said metal oxides being selected from transition metals or from metals of groups IIIA, IVA and VA. This material has a surface area larger than 500 m^2/g, a pore volume between 0.3 and 1.3 ml/g, a pore diameter smaller than 40 Angstrom and an XRD powder spectrum which does not have a crystalline structure, does not show any peak, and has a single broad diffraction line, or, in any case, a widespread scattering at angular values not higher than $2\theta = 5°$ with CuKα radiation, without any other scattering phenomena coherent for higher angular values. By means of the process of the present invention, the selective adsorption of at least one of the gases forming the gaseous mixture, is obtained.

The process is particularly suitable for the sweetening of natural gas, mainly to remove carbon dioxide, hydrogen sulphide or mixtures thereof, from natural gas. The process can also be used in the separation of hydrogen from blends containing carbon dioxide, carbon monox-

ide, hydrogen sulphide, water and hydrocarbons, such as, for example, gaseous effluents from steam methane reforming. In this case, hydrogen is the non-adsorbed component.

The separation of gases in a blend can be effected using various methods. For the removal of nitrogen from natural gas, for example, cryogenic processes, adsorption processes or membrane systems, can be used. In all these processes, the gas is produced at low pressure and must therefore be recompressed to be delivered.

The cryogenic processes are also carried out at low temperatures and therefore require pre-treatment to remove the components present in the natural gas which solidify under these conditions.

In order to separate acid gases such as CO_2 and H_2S from natural gas, systems respectively based on the use of amines, solvents, alkaline solutions of inorganic salts or mixtures thereof, can be used. The acid gases are then eliminated from the solvent by means of high temperature stripping or depressurization. These technologies are typically used for large gas volumes to be treated.

Technologies based on semi-permeable membranes have been proposed for gas separation. In Guoqing Guan et al., Journal of Chemical Engineering of Japan, vol.34, No.8,

pp. 990-997, 2001, for example, the separation of nitrogen from oxygen is described, using membranes containing zeolites of the FAU type.

In the case of the purification of natural gas, membrane systems are used for separating carbon dioxide: the membranes consist of polymer films without pores and extremely dense, in which the carbon dioxide dissolves and is conveyed by diffusion. In US 3,616,607, the use is described of a membrane based on polyacrylonitrile for the separation of N_2/CH_4 with a high selectivity, but low permeability. US 6,565,626 describes a process with organic membranes permeable to CO_2, H_2O, H_2S, N_2, but with a low permeability to CH_4.

The SPREX process allows the extraction of hydrogen sulphide from natural gas streams containing at least 10% by volume of H_2S by cooling the gaseous feeding stream to -30°C or -60°C (Hydrocarbon Processing: Gas Processes 2006, Gulf Publishing Company).

A stream rich in H_2S is thus produced, suitable for being injected again into the gas well, together with a stream rich in CH_4, destined for washing with amines for the abatement of the residual acid gases until the specification required.

Adsorption/desorption cycles are also known, such as, for example, those of the "pressure swing" (PSA), "thermal

swing" (TSA), "vacuum swing" (VSA), "pressure-thermal swing" (PTSA), "pressure-vacuum swing" (PVSA) type.

In particular, gas separation by "pressure swing adsorption" (PSA) is well-known to experts in the field and allows the selective adsorption and separation of the components of a gaseous mixture. The desired product is normally only one of the components. PSA-type processes substantially comprise the following steps:

- a first step in which a gaseous mixture containing two or more gases is put in contact, at high pressure, with an adsorbing material and one or more of the gases forming the mixture are selectively adsorbed; the adsorption normally takes place in short times, in the order of 30 seconds to 5 minutes;
- a subsequent step wherein the adsorbed gas or gases are desorbed by means of one or more of the following systems: pressure lowering, washing with gas. The gas desorption is obtained in this way, and the gas is recovered by regenerating the same adsorbent;
- and a last step, which concludes the cycle, in which the adsorbing bed is pressurized with the gas fed.

Many processes of this type use zeolites as adsorbing material. US 2,882,243, for example, describes the use of zeolite A as adsorbing agent for separating nitrogen and oxygen. US 3,140,933 describes the use of zeolite X, for

the same type of separation. In US 4,925,460, a chabazite exchanged with lithium is used for gas separation.

EP 758561 describes a process for nitrogen adsorption from gaseous streams containing it, by using suitably exchanged zeolites, selected from chabazite, offretite, erionite, levinite, mordenite, zeolite A, zeolite T, EMC-2, ZSM-3, ZSM-18, ZK-5, zeolite L and zeolite beta. The separation of nitrogen from mixtures containing it together with methane is effected in US 6,068,682, using a new molecular sieve containing titanium.

Engelhard Corporation (now BASF Catalysts) applied this material in a process called Molecular Gate, capable of separating nitrogen from methane (US 6,197,092, US 6,444,012). The Molecular Gate process can also be applied to the removal of carbon dioxide from methane (US 6,610,124). EP 1,254,694 describes the use of zeolite X for separating CO_2 and H_2O from air. If necessary, the desorption phase of gases from the adsorber can be effected by thermal treatment (TSA), or by means of a vacuum (VSA). A process is described in WO 2008/00380 for the separation of gases which includes putting a gas mixture in contact with an ESV-type zeolite in order to obtain the selective adsorption of at least one of the gases forming the gaseous mixture.

"Carbogenic" adsorbents are also mentioned for gas

separation. In US 4,521,221 a process based on "carbon molecular sieves" (CMS) is described for the purification of gaseous mixtures containing methane.

In separation processes based on adsorption/desorption cycles many variables are involved and determine their efficacy. The characteristics of the adsorbing material (ex. composition, porosity, surface properties) are at the basis of the separation capacity of the different gas components. Other variables can be important: for example the sensitivity of the adsorbent to humidity can influence the surface reactivity (the hydroxylation degree, for example) or the porosity, or an insufficient stability can prevent the thermal regeneration of the material to eliminate the accumulation of the adsorbed gas. Low recoveries of the desired gas require onerous internal recycling.

It has now been unexpectedly found that certain materials having a high surface area and a narrow pore distribution can be used as adsorbents for the separation of gaseous mixtures providing very high selectivities, even such as to allow the direct use of the gas without requiring subsequent recycling treatment or further purification steps.

These materials can be completely regenerated by means of isothermal depressurization. They are also particularly stable and can therefore undergo thermal treat-

ment with the aim of restoring their adsorbing characteristics. In particular, they have proved to be particularly suitable for "bulk removal" operations of acid gases from natural gas. "Bulk removal" operations specifically consist in the massive removal of pollutants present in natural gas, without necessarily reaching the required specifications, possibly passed on to subsequent "polishing" or finishing treatment (R. Wagner, B. Judd, Gas Sweetening Fundamentals, Proceedings of the 56th Laurance Reid Gas Conditioning Conference, Norman, OK, 2006, 1). The in situ regenerability for many cycles is therefore a main requirement for adsorbents to be used in "bulk removal" operations. Specifically as a result of the high quantities of pollutants to be removed from natural gas, the use of poorly regenerable adsorbers (which are such as to require frequent substitutions) cannot be proposed.

A first object of the present invention therefore relates to a process for gas separation comprising putting a mixture of gas in contact with a porous material in order to obtain the selective adsorption of at least one of the gases forming the gaseous mixture, wherein said material comprising a silica matrix in which one or more metal oxides are possibly uniformly dispersed, selected from transition metals or from metals belonging to groups

IIIA, IVA and VA, characterized by a surface area larger than 500 m^2/g, a pore volume ranging from 0.3 to 1.3 ml/g, a pore diameter lower than 40 Angstrom, an XRD powder spectrum which does not have a crystalline structure, does not reveal any peak, and has a single broad diffraction line, or, in any case, a widespread "scattering", at angular values not larger than $2\theta = 5°$ with CuKα radiation, without any other scattering phenomena coherent for larger angular values.

The remaining gases forming the mixture pass through the adsorbing bed and can therefore be separated. The adsorbed gas(es) are subsequently recovered and/or removed by desorption.

The material used in the process of the present invention, comprising a silica matrix in which one or more metal oxides selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA and having the aforementioned characteristics, are possibly uniformly dispersed, is called ERS-8 and is described in EP 691305, EP 736323 and EP 812804.

These materials preferably have a surface area larger than 800 m^2/g and a pore volume preferably between 0.3 and 0.6 ml/g.

A particular aspect of the present invention is that the metal oxide dispersed in the silica matrix is alumin-

ium oxide: these silico-aluminas of the ERS-8 type preferably have a SIO_2/Al_2O_3 molar ratio higher than 50, even more preferably ranging from 100 to 500.

In accordance with the IUPAC terminology, "Manual of Symbols and Terminology" (1972), Appendix 2, Part I Coll. Surface Chem. Pure Appl. Chem., Vol. 31, page 578, in which pores with a diameter smaller than 20 Angstrom are called micropores, those with a diameter of between 20 and 500 Angstrom are defined mesopores, those with a diameter larger than 500 Angstrom, macropores, the materials of the ERS-8 type used in the present invention and, in particular, silica-aluminas of the ERS-8 type, are micro-mesoporous materials and preferably substantially microporous.

The materials of the ERS-8 type, and in particular silica-aluminas of the ERS-8 type and their preparation are described in EP 691305, EP 736323 and in EP 812804, whose content is incorporated herein as reference, in G. Perego et al. "ERS-8: a new class of microporous aluminosilicates" H. Chon, S. K. Ihm and Y.S. Uh (Editors) Progress in Zeolite and Microporous Materials, Studies in Surface Science and Catalysis, Vol. 105, 1997 Elsevier Science B.V. and in C.Rizzo et al., "Synthesis and textural properties of amorphous silica-aluminas", Studies in Surface Science and Catalysis Volume 128, 2000, Pages

613-622.

In accordance with what is described in EP 691305, for example, the materials of the ERS-8 type of the present invention can be prepared as follows:

(A) a solution of a tetra-alkyl orthosilicate in alcohol is subjected to hydrolysis and gelification with an aqueous solution of a hydroxide of tetra-alkyl ammonium having the formula:

$$R'_4N\text{-}OH$$

wherein R' represents a C_3-C_7 alkyl group or one or more soluble or hydrolyzable compounds of one or more metals selected from transition metals or from metals belonging to groups IIIA, IVA and VA;

the quantity of the constituents of the above solution being such as to respect the following molar ratios:

H_2O/SiO_2 = 5-30

$R\text{-}OH/SiO_2$ = 5-10

R'_4N^+/SiO_2 = 0.05 - 0.5

metal oxides/SiO_2 = 0 - 0.05,

whereas the H_2O/R'_4N^+ ratio varies with a variation in the number of carbon atoms in the alkyl chain R' according to the values shown in Table 1 below:

R'_4N-OH	H_2O/R'_4N^+
Tetra-hexyl-ammonium-hydroxide	≤ 133
Tetra-pentyl-ammonium-hydroxide	≤ 100
Tetra-butyl-ammonium-hydroxide	≤ 73
Tetra-propyl-ammonium-hydroxide	≤ 53

Table 1

operating at a temperature close to the boiling point, at atmospheric pressure, of the alcohol used in the solution of tetra-alkyl-orthosilicate and of any alcohol formed as by-product of the above hydrolysis reaction, with no elimination, or without any substantial elimination of said alcohols from the reaction environment, preferably at a temperature ranging from 20 to 80°C;

(B) subjecting the gel in step (a) to drying and calcination.

The tetra-alkyl orthosilicate can be selected from tetramethyl-, tetraethyl-, tetrapropyl-, tetra-isopropyl-orthosilicate, and tetra-ethyl-orthosilicate (TEOS) is preferred. The alcohol used for solubilizing the above-mentioned tetra-alkyl orthosilicate is preferably ethanol. The soluble or hydrolyzable compounds of one or more metals are selected from the salts or hydrosoluble or hydro-

lysable acids of the same metals. Among these, aluminium tripropoxide and triisopropoxide are preferred. In the case of liquid aluminium alkoxides, it is possible to dissolve these alkoxides in the alcohol solution instead of in the aqueous solution.

Preparations of materials of the ERS-8 type are also described in EP 736323 and EP 812804. In particular, preparations are preferred in which the hydrolysis and gelification step is effected at atmospheric pressure, using reactors equipped with reflux condensers and in the presence of a tetra-alkyl ammonium hydroxide in which at least one of the alkyl substituents contain 6 or 7 carbon atoms.

The materials of the ERS-8 type, in particular silico-aluminas of the ERS-8 type, can be used in the process of the present invention in the form bound with an inorganic binder, selected, for example, from alumina, silica, clay. Binding processes which can be used are those well-known to experts in the field, such as pressing, extrusion, granulation, drop coagulation, atomization techniques. In the final bound product, the material of the ERS-8 type and, in particular, the silico-alumina of the ERS-8 type, is contained in proportions of between 50 and 100% by weight with respect to the total weight of the product, wherein the proportion of 100% refers to a

formation in the absence of a binder. In the final bound product, the material of the ERS-8 type and, in particular, the silico-alumina of the ERS-8 type, is preferably contained in a proportion higher than 80% by weight with respect to the total weight of the product.

The process for the separation of gases of the present invention, which comprises putting a mixture of gases in contact with a material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, so as to have the selective adsorption of at least one of the gases forming the gas mixture, can be effected by means of adsorption/desorption cycles.

According to this latter technology, the gaseous mixture to be fractionated is put in contact with the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, in order to selectively adsorb one or more components of the same mixture. The non-adsorbed component is collected as pure product and the adsorbed components are periodically desorbed, for example by means of reduction in the pressure and/or washing, and/or temperature increase, so as to avoid saturation of the adsorbing bed.

Among processes based on adsorbing/desorbing cycles, those of the "pressure swing" (PSA), "thermal swing" (TSA), "vacuum swing" (VSA), "pressure-vacuum swing" (PVSA) or "pressure-thermal swing" (PTSA) type (D.M. Ruth-

ven, S. Farooq, K.S. Knaebel, Pressure Swing Adsorption (1994) Wiley - VCH) can be well used in the present invention.

In the first case, "pressure swing adsorption", after adsorption at high pressure of at least one of the gases forming the mixture, and the separation of the remaining components of the mixture, the pressure is reduced to de-adsorb the adsorbed gas and regenerate the adsorbing bed containing the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type.

In the case of a TSA process the desorption step is effected, instead of by reducing the pressure, by raising the temperature of the adsorbing bed containing the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type.

In the case of a PTSA process, the adsorption step is carried out at high pressure, whereas the desorption step is effected by increasing the temperature of the adsorbing bed, containing the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, and reducing the pressure.

In the case of a VSA process, the adsorption step is carried out at atmospheric pressure, or slightly higher, whereas the desorption step is effected by reducing the pressure to vacuum.

In the case of a PVSA process, the adsorption step is carried out at high pressure, whereas the desorption step is effected by reducing the pressure to vacuum. A process of the PVSA type is therefore a particular case of the PSA process, in which the desorption is effected under vacuum.

In cases in which the use of a vacuum is not envisaged, the desorption can be facilitated by the contemporaneous washing of the adsorbing bed containing, for example, silico-alumina, by partial recycling of the pure component, not adsorbed, or with inert gas not contained in the feeding.

The process of the present invention is preferably effected by means of "pressure swing adsorption" (PSA) o "pressure-thermal swing adsorption" (PTSA).

A particular aspect of the present invention is therefore a process for the separation of gases of the PSA type comprising the following steps:

a) putting a mixture of gases in contact, under high pressure, with a porous material to selectively adsorb at least one of the gases forming the mixture and collecting or discharging the remaining gaseous components of the mixture, wherein said material includes a silica matrix in which one or more metal oxides selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, are possibly uniformly dispersed,

characterized by a surface area larger than 500 m^2/g, a pore volume between 03 and 1.3 ml/g, an average pore diameter smaller than 40 Angstrom, an XRD powder spectrum which does not have a crystalline structure, does not show any peak and has a single, broad diffraction line, or in any case, a widespread scattering at angular values not larger than $2\theta = 5°$ with CuKα radiation, without any other scattering phenomena coherent for higher angular values;

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing the gas(es) adsorbed in step (a), by reduction of the partial pressure of the gas(es) adsorbed and collecting them or discharging them;

d) re-pressurizing the system with the gas mixture fed.

Accessory operations such as recycling of the products, partial depressurization (in equi- and/or countercurrent with respect to the feed), rinsing of the adsorbing bed, well-known to experts in the field, can be added to phases (a) -(d). According to a preferred aspect, the material of the ERS-8 type used in step (a) is a silicoalumina of the ERS-8 type.

The adsorbing step (a) can be carried out at a temperature ranging from 0 to 40°C, preferably at room temperature, and at an adsorbing pressure of 10 to 90 bara,

preferably 10 to 40 bara.

In step (c) the desorption pressure can be selected from 0.1 to 10 bara, whereas the temperature ranges from 0 to 40°C and is preferably room temperature. When in step (c) the desorption is chosen to be effected under vacuum, the process will be in particular of the PVSA type.

When the process of the present invention is effected by means of PTSA, the adsorption step (a) is carried out under the same conditions described above, whereas the desorption step (c) is effected by means of an increase in the temperature of the adsorbing bed containing the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, and a reduction in the pressure: it is therefore preferable to operate at a pressure ranging from 0.1 to 10 bara and a temperature of 50 to 250°C, even more preferably between 60 and 100°C.

In both PSA and PTSA cases the desorption process and therefore the regeneration of the adsorbing bed containing the material of the ERS-8 type, are favoured by gas rinsing, such as, for example, N_2, CH_4, air or hydrogen.

The process of the present invention can be successfully used, in particular, for the purification of natural gas from pollutants selected from CO_2, H_2S, water and mixtures thereof, wherein the water is in a quantity, at the most, equal to the saturation of the gaseous mixture. The

contaminants are preferably adsorbed with respect to methane. According to a preferred aspect, the process of the present invention is used for the purification of natural gas from CO_2 and/or H_2S. In accordance with the above, a particularly preferred aspect of the present invention is a process of the PSA type for the separation of carbon dioxide, H_2S or mixtures thereof from a gaseous mixture containing them together with methane, comprising the following steps:

a) putting said gaseous mixture in contact with a porous material, at high pressure, in order to selectively adsorb carbon dioxide, H_2S or their mixture, and collecting the remaining gaseous component containing methane, wherein said material comprises a silica matrix in which one or more metal oxides selected from transition metals or metals belonging to groups IIIA, IVA and VA, are possibly uniformly dispersed, characterized by a surface area larger than 500 m^2/g, a pore volume ranging from 0.3 to 1.3 ml/g, an average pore diameter smaller than 40 Angstrom, an XRD powder spectrum which does not have a crystalline structure, does not show any peak, and has a single broad diffraction line, or, in any case, a widespread scattering at angular values not higher than $2\theta = 5°$ with CuKα radiation, without any other scattering phenomena coherent for higher angular values.

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing carbon dioxide, H_2S or their mixture, adsorbed in step (a), by reduction of the partial pressure of the gas or gases adsorbed, collecting or discharging them;

d) re-pressurizing the system with the gas mixture fed.

In step (a), a silico-alumina is preferably used as adsorbing material of the ERS-8 type. If the separation of carbon dioxide, H_2S or a mixture thereof, from a gaseous mixture containing them together with methane, is carried out by means of PTSA, the desorption step (c) is effected by an increase in the temperature of the adsorbing bed containing the material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, and reduction of the pressure.

The same general pressure and temperature conditions described above are applied to the separation of natural gas from pollutants selected from CO_2, H_2S, water and mixtures thereof, by means of a process of the PSA or PTSA type.

In particular, by using a material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type in a PSA process, it is possible to abate the content of acid

gases in natural gas from 20% by volume to less than 2% by volume, with a methane recovery, expressed as CH_4 in the stream of sweetened gas, referred to the quantity of CH_4 in the stream of gas to be treated, of at least 80%.

The material of the ERS-8 type, preferably a silico-alumina of the ERS-8 type, when used in the present gas adsorption process, in particular when used for the removal of acid gas, can be completely regenerated by isothermal depressurization and a particularly preferred aspect of the present invention is therefore to effect the desorption step of the adsorbed gases by reducing the partial pressure of the adsorbed gas(es), at a constant temperature.

The materials of the ERS-8 type, used in the separation process of the present invention and preferably silico-aluminas of the ERS-8 type, unexpectedly prove to be capable of contemporaneously satisfying the following requirements, with particular reference to CO_2:

a) maximum quantity of adsorbable CO_2 at 5 bara and 30°C, higher than 50 Nml/g;

b) ratio between the maximum quantity of adsorbable CO_2 and CH_4 at 5 bara and 30°C, higher than 3.5:

c) maximum quantity of CO_2 that can be released by isothermal depressurization from 5 bara to 0.5 bara at 30°C, equal to at least 75% of the maximum quantity ad-

sorbable at 5 bara.

With particular reference to H_2S, the materials of the ERS-8 type and, preferably, a silico-alumina of the ERS-8 type, used in the separation process of the present invention are capable of contemporaneously satisfying the following requirements:

a) maximum quantity of adsorbable H_2S at 5 bara and 30°C, higher than 120 Nml/g;

b) ratio between the maximum quantity of adsorbable H_2S and CH_4 at 5 bara and 30°C, higher than 8.5:

c) maximum quantity of H_2S that can be released by isothermal depressurization from 5 bara to 0.5 bara at 30°C, equal to at least 75% of the maximum quantity adsorbable at 5 bara.

The process of the present invention can also be used for the separation of hydrogen from mixtures containing carbon dioxide, carbon monoxide and hydrocarbons, such as, for example, gaseous effluents from "steam methane reforming". In this case, hydrogen is the non-adsorbed component.

In the following examples, according to the present invention, the results of the experimental tests are expressed by using, as measurement parameter of the adsorbing properties of a material, the adsorption capacity at equilibrium q(Nml/g), expressed as the quantity of ad-

sorbed gas at equilibrium under certain conditions (T, P) and referring to the weight of the adsorbing material (specific capacity). The function q(Nml/g) = f(T, p) is commonly referred to as adsorption/desorption isotherm.

The following examples have the sole purpose of describing the present invention in greater detail and should not be interpreted as limiting the objectives of the same.

Example 1 - synthesis of ERS-8 silico-alumina

669.2 g of tetra-hexyl ammonium hydroxide at 40% by weight in aqueous solution are diluted with 928.4 g of water and charged into a reactor equipped with a condenser. A solution containing 1667.0 g of tetra-ethyl orthosilicate, 2944.0 g of ethanol and 13.2 g of aluminium sec-butoxide are added at room temperature, and the whole mixture is maintained under stirring for 3 hrs. A limpid sol is obtained which is concentrated in a rotavapor until a gel is formed. The gel is dried under vacuum at 80°C and calcined at 550°C for 8 hrs.

The material obtained was characterized by adsorption of N_2 at -196°C:

- specific surface area (BET method): 1260 m^2/g;
- pore volume (Gurvitsch rule): 0.6 cm^3/g;
- average pore diameter (DFT method): 16 Angstrom.

Example 2 - Absorption test with ERS-8 silico-alumina

The adsorbing material of Example 1 was pre-treated under vacuum at 350°C for 16 hrs and the adsorption/desorption isotherms were acquired on it for H_2S, CO_2, CH_4 at 30 °C. The results are shown in Figure 1. From Figure 1 it can be seen that the adsorbing material synthesized according to Example 1 preferably adsorbs the acid gases (H_2S and CO_2) with a high selectivity with respect to CH_4, within a wide pressure range.

A high selectivity prevents the co-adsorption of various components on the same adsorbing material, thus increasing the efficiency of the separation process.

In the case of the sample of Example 1, the quantities of CO_2, H_2S and CH_4 adsorbed at 5 bara and 30°C are 57 Nml/g, 132 Nml/g and 14 Nml/g respectively. It follows that the ratio between the maximum quantity of CO_2 and CH_4 which can be adsorbed by the sample of Example 1 (at 5 bara and 30°C) is equal to 4, whereas the ratio between the maximum quantity of H_2S and CH_4 which can be adsorbed by the sample of Example 1 (at 5 bara and 30°C) is equal to 9.5.

It can also be noted that the quantity of acid gas (H_2S and CO_2) which can be adsorbed by the adsorbing material is strongly correlated with the pressure. This makes these adsorbing materials easily regenerable by depressurization and/or washing with gas (CH_4, N_2, for ex-

ample). Regenerability is a necessary characteristic for an adsorbing material to be used in a cyclic separation process.

In the case of the sample of ERS-8 silico-alumina of Example 1, by depressurization to 0.5 bara under isothermal conditions, the adsorbing material releases about 80% of the acid gas (H_2S and CO_2) adsorbed at 5 bara at 30°C.

Example 3

In this example, the behaviour is described of the adsorbing material synthesized as described in Example 1, in the competitive adsorption of CO_2.

A tubular adsorber was charged with the adsorbing material granulated at 20-40 mesh.

The adsorber was degassed *in situ* at 350°C under vacuum for 16 hrs.

After waiting for the system to be cooled to stabilization of the pre-established temperature, a gaseous mixture having a composition of $CH_4/CO_2/N_2$ = 60/27/13 (% vol.), was fed to the adsorber.

The following adsorption operative conditions were used:

T = 27°C

p = 30 barg.

Gas-chromatographic analyses effected on the effluent from the adsorber revealed a reduction of the CO_2 content

to less than 2.5% by volume for more than 20 minutes and the re-establishment of a CO_2 concentration identical to that in the feeding after about 35 minutes.

On the whole, the CO_2 adsorption, referring to the weight of adsorbing material, proved to be equal to 90 Nml/g.

This value is comparable to the equilibrium value (obtained from the measurements described in Example 2, carried out with pure CO_2) and indicates the selectivity of the adsorbing material. Also in the presence of a large excess of CH_4 in the feeding gas, in fact, it tends to preferably adsorb CO_2.

Example 4

In this example, the regeneration of the adsorbing material synthesized as described in Example 1 is indicated, by means of depressurization and washing of the adsorbing bed with CH_4.

After an adsorption under pressure carried out according to the procedure described in Example 2, the adsorbing bed was regenerated *in situ*.

The operation was carried out by depressurization and subsequent sweeping of the adsorbing bed with CH_4.

The following operative conditions were adopted for the regeneration:

T = 27°C

p = 3 barg.

In order to evaluate the regenerability of the adsorbing bed, 5 adsorption/desorption cycles were repeated according to the above-mentioned procedures.

Table 2 shows the quantities of CO_2 adsorbed (referring to the weight of the adsorbing material) during the cycles.

Example 5

This example describes the effect of the thermal regeneration of the adsorbing material synthesized as described in Example 1.

At the end of the 5 adsorption/desorption cycles, mentioned in Example 4, the adsorbing material saturated with CO_2 was treated at 350°C under a stream of CH_4, *in situ*. At the end of the thermal regeneration, after cooling the system to room temperature, the sequence of 5 adsorption/desorption cycles was repeated with the same procedures described in Example 4.

	Example 4	Example 5
Cycles	CO_2 Ads.	CO_2 Ads.
	[Nml / g]	[Nml / g]
1	90	89
2	89	91
3	90	90
4	91	90
5	90	90

Table 2

From Table 2 the following can be observed:

- the adsorbing material synthesized as described in Example 1 can be regenerated by depressurization and sweeping with CH_4. No significant decrease in the specific capacity for CO_2 is revealed during the 1-5 cycles.
- the adsorbing material synthesized as described in Example 1, can be regenerated by thermal treatment. No significant decrease in the specific capacity for CO_2 is revealed passing from the 5 cycles of Example 4 to the 5 cycles of Example 5.

Example 6 (comparative) - Adsorption test with a commercial adsorbent.

An adsorbing test is carried out on a sample of commercial adsorbing material (Grace Davison SG125 silica)

whose morphological characteristics (determined by adsorption of N_2 at -196°C) are indicated hereunder:

- specific surface area (BET method): 725 m^2/g;
- pore volume (Gurvitsch rule): 0.38 cm^3/g;
- average pore diameter (DFT method): 16 Angstrom.

The adsorbing material was pretreated under vacuum at 350°C for 16 hrs and the adsorption/desorption isotherms of H_2S and CO_2 were acquired on this at 30 °C. The results are indicated in Figure 2.

From the data shown in Figure 2 it can be seen that the specific capacity, respectively for H_2S and CO_2, of the commercial material is lower than that indicated in Figure 1 for the silico-alumina of the ERS-8 type .

The specific capacity represents a fundamental characteristic for an adsorbing material to be used in a cyclic separation process. In particular, high specific capacities allow less frequent regenerations of the adsorbing material used.

Example 7

This example describes the behaviour of the adsorbing material synthesized as described in example 1, in the competitive adsorption of H_2S.

A tubular adsorber was charged with the adsorbing material granulated at 20-40 mesh.

The adsorber was degassed *in situ* at 350°C under vac-

uum for 16 hrs.

After waiting for the system to be cooled to stabilization of the pre-established temperature, a gaseous mixture having a composition of CH_4/H_2S = 90/10 (% vol.), was fed to the adsorber.

The following adsorption operative conditions were used:

T = 27°C

p = 30 barg.

Gas-chromatographic analyses effected on the effluent from the adsorber revealed a reduction of the H_2S content to less than 500 ppmv in the phases preceding the saturation of the bed.

On the whole, the H_2S adsorption, referring to the weight of the adsorbing material, proved to be equal to 90 Nml/g.

This value is comparable to the equilibrium value (obtained from the measurements described in Example 2, carried out with pure H_2S) and indicates the selectivity of the adsorbing material. Also in the presence of a large excess of CH_4 in the feeding gas, in fact, it tends to preferably adsorb H_2S.

Example 8

This example indicates the regeneration of the adsorbing material synthesized as described in Example 1 by means

of depressurization and washing of the adsorbing bed with CH_4.

After an adsorption under pressure carried out according to the procedure described in Example 7, the adsorbing bed was regenerated *in situ*.

The operation was carried out by depressurization and subsequent sweeping of the adsorbing bed with CH_4.

The following operative conditions were adopted for the regeneration:

T = 27°C

p = 3 barg.

In order to evaluate the regenerability of the adsorbing bed, 5 adsorption/desorption cycles were repeated according to the above-mentioned procedures.

Table 3 indicates the quantities of H_2S adsorbed (referring to the weight of the adsorbing material) during the cycles.

	Example 8
Cycles	**H_2S Ads.**
	[Nml / g]
1	90
2	89
3	89
4	91
5	90

Table 3

From the data indicated in Table 3 it can be deduced that the adsorbing material synthesized as described in Example 1, can be regenerated by depressurization and sweeping with CH_4. No significant decrease in the specific capacity of H_2S is observed within the sequence of the cycles 1-5. In addition, the regeneration carried out without the application of vacuum, allows the possible costs due to the recompression of the stream rich in acid gas, to be limited, in the possibility of re-injection into the well, related to "enhanced hydrocarbon recovery" operations.

CLAIMS

1) Process for the separation of gases comprising placing a gaseous mixture in contact with a porous material to obtain the selective adsorption of at least one of the gases making up the gaseous mixture, wherein said material comprising a silica matrix in which one or more metal oxides are possibly dispersed, in a uniform manner, selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crystalline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread "scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values.

2) Process according to claim 1 comprising a desorption step of the adsorbed gases.

3) Process according to claim 1 wherein the pore volume of the porous material is in the range of 0.3 - 0.6 ml/g.

4) Process according to claim 1 wherein the surface area of the porous material is greater than 800 m^2/g.

5) Process according to one or more of the preceding claims wherein the metal oxide dispersed in the silica matrix, contained in the porous material, is aluminium oxide.

6) Process according to the preceding claim wherein the molar ratio between the aluminium oxide and the silica of the matrix contained in the porous material is greater than 50.

7) Process according to one or more of the preceding claims wherein the porous material is in a bound form with an inorganic binder.

8) Process according to claim 1 implemented through adsorption cycles.

9) Process according to claim 8 implemented through adsorption cycles of the pressure swing adsorption (PSA), thermal swing adsorption (TSA), vacuum swing adsorption (VSA), pressure-thermal swing adsorption (PTSA), or pressure-vacuum swing adsorption (PVSA) type.

10) Process according to claim 9 implemented through adsorption cycles of the PSA or PTSA type.

11) Process of the PSA type according to claim 10 comprising the following steps:

a) placing a gaseous mixture in contact, under high pressure, with a porous material to obtain the selective adsorption of at least one of the gases making up the gase-

ous mixture and collecting or discharging the remaining gaseous components of the mixture, where said porous material comprises a silica matrix in which one or more metal oxides are possibly dispersed, in a uniform manner, selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crystalline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread "scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values;

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing the gas or gases adsorbed in step (a), by reducing the partial pressure of the adsorbed gas or gases, and collecting or discharging them;

d) repressurizing the system with the gaseous mixture fed.

12) Process of the PTSA type according to claim 10 comprising the following steps:

a) placing a gas mixture in contact, under high pressure,

with a porous material to obtain the selective adsorption of at least one of the gases making up the gaseous mixture and collecting or discharging the remaining gaseous components of the mixture, where said porous material comprising a silica matrix in which one or more metal oxides are possibly dispersed, in a uniform manner, selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crystalline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread "scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values;

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing the gas or gases adsorbed in step (a),by raising the temperature of the porous material and reducing the partial pressure of the adsorbed gas or gases, and collecting or discharging them;

d) repressurizing the system with the gas mixture fed.

13) Process according to claim 1 wherein the gaseous mixture is natural gas containing one or more pollutants selected from among CO_2, H_2S, water, which are adsorbed.

14) Process according to claim 1 wherein the gaseous mixture is hydrogen containing carbon dioxide, carbon monoxide, hydrogen sulphide, water and hydrocarbons which are adsorbed.

15) Process according to claim 11 or 13 of the PSA type for separating a pollutants from a gaseous mixture which contains it together with methane, where said pollutant is CO_2, H_2S or their mixtures, comprising the following steps:

a) placing said gaseous mixture in contact, under high pressure, with a porous material to selectively adsorb the pollutant, and collecting the remaining gaseous component containing methane, where said porous material comprising a silica matrix in which one or more metal oxides are possibly dispersed, in a uniform manner, selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crystalline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread

"scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values;

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing the pollutant adsorbed in step (a), by reducing the partial pressure of the adsorbed gas or gases, and collecting or discharging them;

d) repressurizing the system with the gas mixture fed.

16) Process according to claim 12 or 13 of the PTSA type for separating a pollutants from a gaseous mixture which contains it together with methane, where said pollutants is CO_2, H_2S or their mixtures, comprising the following steps:

a) placing said gaseous mixture in contact, under high pressure, with a porous material to selectively adsorb the pollutant, and collecting the remaining gaseous component containing methane, where said porous material comprises a silica matrix in which one or more metal oxides are possibly dispersed, in a uniform manner, selected from among transition metals or from among metals belonging to groups IIIA, IVA and VA, characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crys-

talline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread "scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values;

b) interrupting the flow of the gaseous mixture and possibly reducing the pressure;

c) desorbing the pollutants adsorbed in step (a), by raising the temperature of the porous material and reducing the partial pressure of the gas or the adsorbed gases, and collecting or discharging them;

d) repressurizing the system with the gas mixture fed.

17) Process according to claim 1, 11, 12, 15 or 16 wherein the adsorption is performed at a temperature in the range of 0 - 40°C and at a pressure in the range of 10 - 90 bara.

18) Process according to claim 17 wherein the adsorption is performed at an adsorption pressure in the range of 10 - 40 bara.

19) Process according to claim 2, 11 or 15 wherein the desorption stage is performed at a pressure in the range of 0.1 - 10 bars and at a temperature in the range of 0 - 40 °C.

20) Process according to claim 2, 12 or 16 wherein the desorption stage is performed at a pressure in the range

of 0.1 - 10 bara and heating at a temperature in the range of 50 - 250°C.

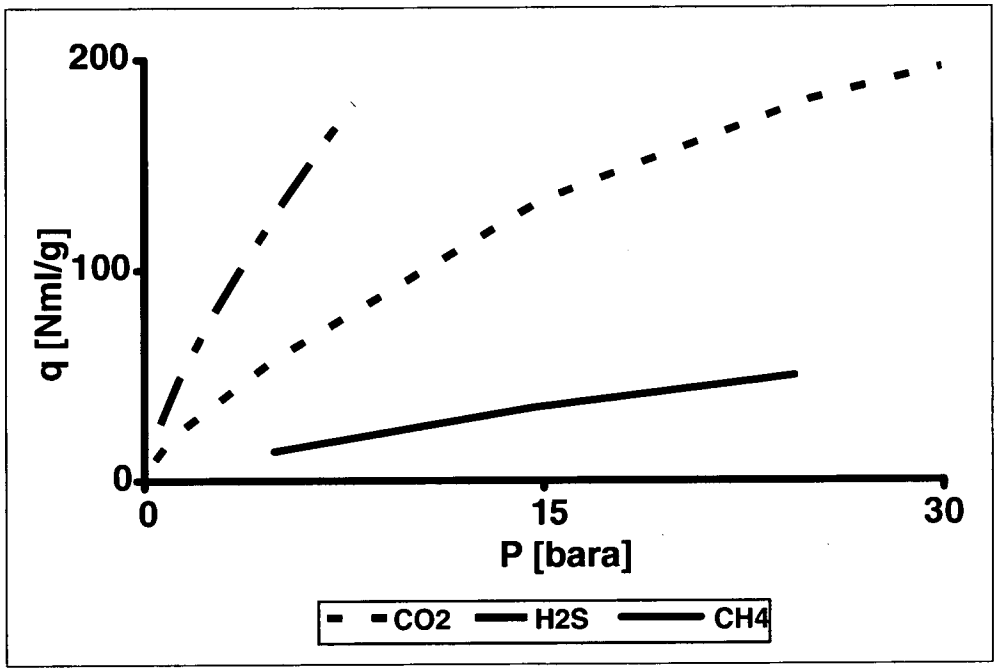
21) Process according to claim 20 wherein the temperature is in the range of 60 - 100 °C.

22) Process according to claim 2, 11, 12, 15 or 16 wherein the desorption is followed by sweeping with a gas selected from among N_2, CH_4, air or hydrogen.

23) Process according to one or more of the claims wherein the porous material comprises a silica matrix in which aluminium oxide is dispersed, and it is characterised by a surface area greater than 500 m^2/g, a pore volume in the range of 0.3 - 1.3 ml/g, a pore diameter smaller than 40 Angstrom, an XRD spectrum from powders not having a crystalline structure, does not show any peak, and has a single broad diffraction line, or in any case a widespread "scattering", at angular values not greater than $2\theta = 5°$ with CuKα radiation, without any other coherent "scattering" phenomena coherent for greater angular values.

24) Process according to claim 1 or 2 wherein the adsorbing porous material is completely regenerated through isothermal depressurization.

Fig. 1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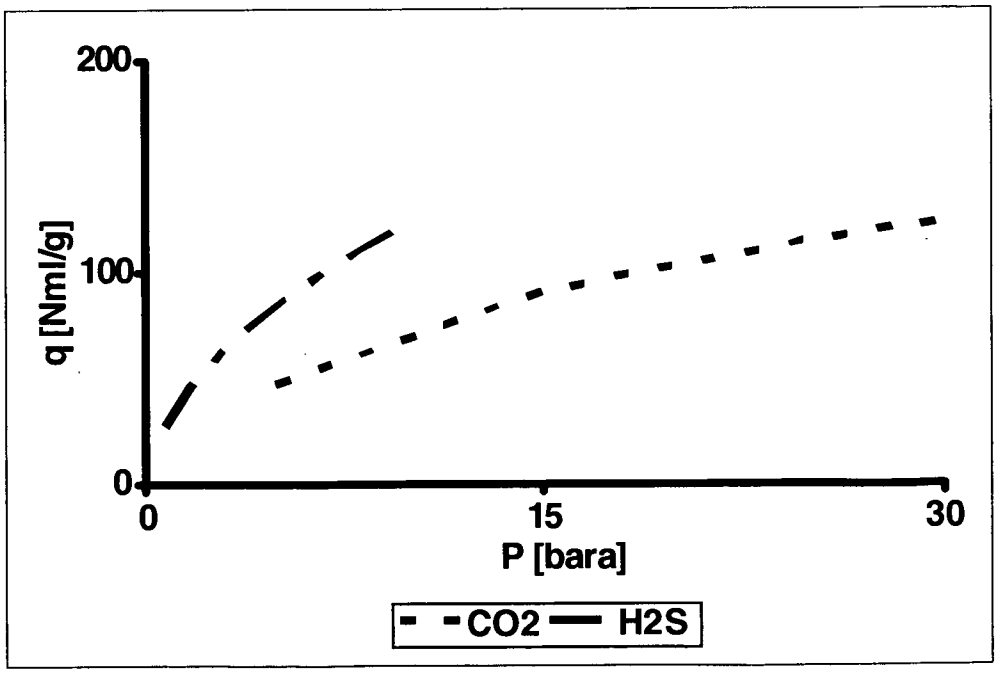
q [Nml/g]
0
15
30
P [bara]
CO2
H2S
CH4

Fig. 2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100
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q [Nml/g]
0
15
30
P [bara]
CO2
H2S