

Gas purification process

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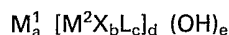
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(71) Applicant Shell Internationale Research Maatschappij B V, (Netherlands), Carel van Bylandtlaan 30, The Hague, The Netherlands	(56) Documents cited None
(72) Inventors Gosse Boxhoorn, Jan Kuyper, Jan Moolhuysen, Rutger Anthony van Santen	(58) Field of search C5E B1L
(74) Agent and/or Address for Service D. A. H. Bennett, 4 York Road, London SE1 7NA	

(54) **Gas purification process**

(57) Process for purifying alkane-containing feed streams by contacting them with one or more metal complexes with intra-crystalline channels according to the general formula:



wherein M¹ represents at least one metal from Group 1b, 2a, 2b, 4a, 7b and/or the nm-noble metals of Group 8; M² represents at least one metal from Group 6b, 7b and/or 8; X represents an (iso)ciano-, and/or (iso)cyanato- and/or (iso)thiocyano-moiety; L represents a nitroso-, an ammino- and/or a halide-moiety, a, b, c, d and e (when OH is present) provide the electroneutrality; and c and e may equal 0.

Compounds such as magnesium hexacyano cobaltate and zinc hydroxy hexacyano cobaltate can be used advantageously in the purification of methane by selectively adsorbing carbon dioxide present therein.

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SPECIFICATION

Gas purification process

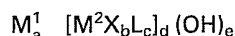
5 The present invention relates to a process for purifying alkanes comprising feed streams by selective adsorption of adsorbable compounds present therein and to purified alkanes comprising gases thus obtained. 5

It is known to use molecular sieves, e.g. zeolites having intra-crystalline channels, in adsorption processes for the separation of non-hydrocarbon components (e.g. CO₂, H₂S, HCN, NH₃, H₂, COS, CO and/or H₂O) from an alkane comprising feed stream such as natural gas. Before adsorption of adsorbable compounds (i.e. 10 compounds having molecules with a kinetic diameter smaller than the width of the intra-crystalline channels in the appropriate molecular sieves) will take place to any substantial extent molecular sieves normally have to be at least partially dehydrated, usually at temperatures substantially above the temperatures at which the adsorption takes place. 10

15 On the one hand, a low dehydration temperature would be attractive from a process point of view, leading to reduced energy consumption and short dehydration periods. On the other hand, it is desirable to use adsorbents with a high decomposition temperature when hot gas streams are to be treated in adsorption processes. Furthermore, the adsorption capacity should be high for the compounds(s) to be adsorbed and low for the other compound(s) present in the feed stream; moreover the adsorption should be reversible, i.e. 20 desorption should be possible without noticeable changing the properties of the adsorbent after a number of adsorption/desorption cycles. On balance, it would be advantageous when the properties of adsorbents could be influenced in such a manner that adsorption processes can be carried out efficiently with a wide range of adsorbable compounds. 20

It has now surprisingly been found that certain metal complexes with adjustable properties, e.g. the 25 geometry and dimensions of the pore system present in such complexes, can be successfully applied in adsorption processes for the purification of alkanes-comprising feed streams. 25

The invention therefore relates to a process for purifying alkanes comprising feed streams by selective adsorption of adsorbable compounds present therein which comprises contacting the feed stream with one or more metal complexes with intra-crystalline channels according to the general formula: 30



wherein M¹ represents at least one metal from Group 1b, 2a, 2b, 4a, 7b and/or the non-noble metals from Group 8 of the Periodic System of Elements; M² represents at least one metal from Group 6b, 7b and/or 8; X 35 represents a(n) (iso)cyno- and/or a(n) (iso)-cyanato- and/or a(n) (iso)thiocyano-moiety; 35

L represents a nitroso-, an ammino- and/or a halide-moiety;

a, d and e are numbers to satisfy the valency state of M¹ and [M²X_bL_c] in the general formula; b and c are integers (b > c) which with a and d, together with e (when OH is present), provide the electroneutrality of the general formula. 40

The Periodic System of Elements referred to is stated in the "Handbook of Chemistry and Physics", 55th edition, CRC Press, Ohio, USA (1975). 40

In the process according to the present invention suitably use is made of metal complexes with intra-crystalline channels according to the general formula wherein M¹ represents at least one of Cu, Ag, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, Mn, Fe, Co or Ni; M² represents at least one of Cr, Mn or the metals from Group 45 8; X represents a cyano moiety; L represents a nitroso moiety; a, b, d and e are numbers which together provide the electroneutrality of the general formula, 45

whereby a is a number from 1-5;

b is 4, 5 or 6;

c is 0, 1 or 2, the sum of b and c being 6;

d is a number from 1-3, and 50 e is a number from 0-2. 50

In the general formula M¹ preferably represents Mg, Zn or Co(II); M² preferably represents Co(III) or Fe(III), whereby

a is 1, 2 or 3;

b is 5 or 6; 55 55

c is 0 or 1;

d is 1 or 2; and

e is 0 or 1.

Most preferably M² represents Co(III).

60 Without wishing to be bound to any particular theory, it would appear that the number of vacancies in the crystal lattices of the metal complexes is a relevant parameter with regard to the possible variation of the width of the intra-crystalline channels present in the presently applied metal complexes. When there are no vacancies in the lattice, narrow channels will be present in such metal complexes, which makes it possible to separate molecules with small kinetic diameters (e.g. in the order of 0.2-0.3 nm) from feed streams 65

65 comprising mostly molecules with kinetic diameters larger than the width of the intra-crystalline channels. In 65

the present process preferably use is made of metal complexes having of from 0 to 50 % vacancies in their crystal lattice, based on the total number of cationic positions in the unit cell of a crystal lattice. Suitable metal complexes possess intra-crystalline channels having a width of from 0.2 to 0.8 nm, and preferably of from 0.3 to 0.6 nm; such metal complexes may be used to adsorb a wide range of compounds according to size, e.g. CO₂, CO, COS, H₂S, HCN, H₂, NH₃, N₂, O₂, H₂O and/or various hydrocarbon molecules with 1-8 carbon atoms. 5

The metal complexes may be prepared from the appropriate components in solution or in suspension; water, lower alcohols, such as methanol and ethanol, and alcohol/water mixtures may be used for this purpose. However, preferably use is made of aqueous solutions and/or suspensions, thus preparing metal silicates comprising up to 20 water molecules per M²-moiety. Before such metal silicates are used in the present process, they are suitably dried, whereby solvent molecules are at least partially removed from the metal complexes. 10

An excellently suitable metal complex for use in the process according to the present invention is magnesium hexacyano cobaltate (MHC).

15 A gaseous feed stream mainly comprising methane and carbon dioxide may be purified using MHC, thus combining a low dehydration temperature, a high ratio of the carbon dioxide/methane adsorption capacities and fast carbon dioxide desorption. The adsorption process is found to be reversible without noticeable changes in the metal complex. Partial dehydration, which is also a reversible process, is suitably carried out by drying MHC at a temperature in the range of from 100 to 200 °C, in particular of from 110 to 160 °C. 15

20 Zinc hydroxy hexacyano cobaltate, Zn₂[Co(CN)₆]OH, (ZHHC) is an example of a metal complex which can be dehydrated at even lower temperatures than MHC, e.g. at a temperature in the range of from 0 to 50 °C. This metal complex is very suitable for use as adsorbent in processes using a low dehydration temperature, especially because of the high ratio of carbon dioxide/methane adsorption capacities of ZHHC. 20

Although it is possible to mix metal complexes in the form of powder into the feed stream and filter the powder out after adsorption of particular feed compounds, for most applications separation is more conveniently carried out in a fixed bed of adsorbent particles comprising the metal complexes. The adsorbent particles may consist of one or more of the above-described metal complexes as such; alternatively these particles may comprise additional components, such as inert binders (e.g. clays or refractory oxides). It is also possible to apply adsorbent particles consisting of carrier material which has been at least partially coated with one or more of the metal complexes used in the present process. 25

30 The adsorbent particle size, shape and strength co-determine the overall characteristics of an adsorbent bed and the mechanical attrition resistance thereof. Premature degradation of the adsorbent particles will produce a fine powder which increases the pressure drop through the bed. In the present process metal complexes-comprising particles are suitably used having a diameter of from 0.1 to 30 mm; the bulk crush strength of these particles is preferably from 0.5-4 MPa. Generally, the use of particles with a smallest size of less than 0.1 mm would lead to an excessive pressure drop over the beds and a tendency to plug readily, whereas the use of particles having dimensions above 30 mm would result in less than optimum use of the available adsorbent volume. Particularly preferred particles comprising the metal complexes are extrudates or spherical particles with a diameter of from 1 to 25 mm. 30

40 A fixed bed-type adsorption process is generally operated in a semi-continuous manner by using at least two adsorbent-comprising beds. While one bed is used for the adsorbing phase of a process cycle, at least one other bed is in the desorbing phase and the desorbed component is subsequently removed from the desorbing bed, rendering it suitable again for use as adsorption bed. When a separate purging phase is part of a process cycle, preferably at least three metal complexes-comprising beds are used of which during a process cycle at least one bed is in the purging phase, thus being desorbed. The usual configuration of the beds is vertical and flow through the beds may be either up or down. 45

Various process cycles may in general be applied in the present process, e.g. the pressure swing-, thermal swing-, purge gas stripping- and displacement cycle.

50 The present process is suitably carried out in a pressure swing cycle operating at essentially isothermal conditions between two pressures, the higher of which is the adsorption pressure. In general pressure swing cycles may operate between super-atmospheric and atmospheric pressures; additional adsorbate may be recovered by vacuum desorption. 50

55 An important advantage of the pressure swing cycle is that in general no heating and cooling steps are involved; consequently the cycle time may be short, e.g. from 0.1 to 30 minutes, thereby enabling a reduction in size of the adsorbent bed in comparison with the application of other types of process cycles. The main source of energy in such a process cycle is gas compression. Other advantages of the pressure swing cycle are the possibility to obtain a high purity product directly from the desorbing bed without distillation or other additional costly separation steps and a low hold-up of feed in the macropores and interparticulate space, compared with liquid phase processes. 55

60 Suitable conditions for carrying out the present process are a temperature between the condensation temperature of a gaseous feed stream and the decomposition temperature of the adsorbent, preferably of from -70 °C to 300 °C, and a total pressure of from 0.1 to 1000 bar, preferably of from 1 to 200 bar. 60

65 The metal complexes used as adsorbent in the process according to the present invention may be prepared by any manner known in the art. It appears that heating of some of these metal complexes may lead to modification of their crystal lattice (e.g. from cubic to rhombohedral) and channel structure. 65

Rhombohedral $Zn_3[Co(CN)_6]_2 \cdot nH_2O$ may be prepared by adding an aqueous solution of an alkali metal salt of the hexacyano cobaltate complex to a stirred aqueous solution of a zinc halogenide and subsequently heating the reaction mixture to a temperature between 70 °C and the boiling point of the mixture for 1-60 minutes. After filtration, the resultant solids may be washed with water and dried at temperatures of from 50-200 °C. Zinc hydroxy hexacyano cobaltate (ZHHC) according to the formula $Zn_2[Co(CN)_6]OH \cdot nH_2O$ (whereby n is 1 or 2) may be obtained by heating an aqueous suspension of zinc hexacyano cobaltate (ZHC), which is preferably prepared in situ in the suspension, and zinc hydroxide at temperatures up to 100 °C, filtering off the precipitate and drying in air.

Magnesium hexacyano cobaltate (MHC) may be prepared by mixing ZHC with an aqueous suspension of magnesium hydroxide, stirring the mixture at room temperature for 0.1-24 hours, filtering off the resultant precipitate and recovering the MHC thus formed, for example by means of film evaporation.

The invention is illustrated by the following Example.

Example

ZHC, MHC and ZHHC, which were prepared as described hereinabove, were evaluated by means of adsorption measurements together with the other metal complexes listed in Table I, which were prepared in a similar manner. All metal complexes were substantially dehydrated at the temperatures indicated in Table I (measured under a nitrogen atmosphere with a thermoanalyser) before the respective adsorption capacities for carbon dioxide and methane for particles of the sieve fraction 0.18-0.59 mm were measured separately at a temperature of 22 °C and a pressure of 1 bar, using a microbalance.

The crystal structure of the metal complexes used in the particles was determined after their synthesis, before (partial) dehydration, by X-ray diffraction.

TABLE I

adsorbent	structure	tempera- ture (°C) for: dehydration	decom- position	adsorption capacity (mmol/g)	
				CO ₂	CH ₄
Mg ₃ [Co(CN) ₆] ₂	cubic	150	615	3.6	0.7
Zn ₃ [Co(CN) ₆] ₂	cubic	310	640	1.5	0.4
Zn ₃ [Co(CN) ₆] ₂	rhombohedral	175	640	1.8	0.4
Co ₃ [Co(CN) ₆] ₂	cubic	111	>480	2.9	0.5
Zn[Fe(CN) ₅ NO]	cubic	20	430	1.9	0.4
Zn ₂ [Co(CN) ₆]OH	hexagonal	110	470	2.5	0.9
Zn ₂ [Co(CN) ₆]OH	not determined	20	470	2.7	0.4
Fe ₄ [Fe(CN) ₆] ₃	cubic	150	130	1.1	0.2

From the results given in Table I it will be clear that magnesium hexacyano cobaltate, which has the highest adsorption capacity for carbon dioxide, in combination with an acceptable ratio of carbon dioxide and methane adsorption capacities, is very suitable for use as adsorbent in a process for purifying a methane-comprising feed stream. Moreover, MHC can be used at high temperatures, if necessary, because substantial decomposition does not occur below 615 °C, whereas its dehydration temperature is conveniently low.

MHC was further tested by varying the temperatures (T_{ads}) and pressures at which the adsorption capacities for carbon dioxide and methane were determined, using for the measurements at 10 bar a tube of 5 ml volume, filled with partially dehydrated MHC of which the weight increase after saturation was measured by means of an analytical balance; all other measurements were carried out as described hereinabove. In addition, a gas mixture comprising carbon dioxide and methane in a molar ratio of 1, was used as feed. The results are given in Table II.

TABLE II

Gas	Pressure (bar)	T_{ads} (°C)	adsorption cap. (mmol/g)
CO ₂	10	20	5.4
	1	-42	6.1
	1	20	3.6
	0.5	-42	5.5
	0.5	20	2.6
	10	20	1.6
CH ₄	1	20	0.7
	0.5*	-42	6.7**
	0.5*	20	2.5**
CO ₂ /CH ₄ (ratio 1)	0.5*	20	2.5**

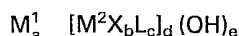
* partial pressure of carbon dioxide; total pressure 1 bar.

** adsorption capacity for carbon dioxide and methane combined.

The results given in Table II indicate that the adsorption capacity of MHC for carbon dioxide increases with higher operating pressures and with lower adsorption temperatures; the adsorption capacity of MHC is still excellent when a carbon dioxide/methane 1:1 mixture is applied as feed.

CLAIMS

1. Process for purifying alkanes comprising feed streams by selective adsorption of adsorbable compounds present therein which comprises contacting the feed stream with one or more metal complexes with intra-crystalline channels according to the general formula: 10



15 wherein M^1 represents at least one metal from Group 1b, 2a, 2b, 4a, 7b and/or the non-noble metals from Group 8 of the Periodic System of Elements; M^2 represents at least one metal from Group 6b, 7b and/or 8; X represents a(n) (iso)cyno- and/or a(n) (iso)cyanato- and/or a(n) (iso)thiocyano-moiety; 15

L represents a nitroso-, an amino- and/or a halide-moiety;

a, d and e are numbers to satisfy the valency state of M^1 and $[M^2X_bL_c]$ in the general formula; b and c are integers ($b > c$) which with a and d, together with e (when OH is present), provide the electroneutrality of the general formula. 20

2. Process according to claim 1, wherein use is made of metal complexes according to the general formula wherein M^1 represents at least one of Cu, Ag, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Sn, Pb, Mn, Fe, Co or Ni; M^2 represents at least one of Cr, Mn or the metals from Group 8; X represents a cyano moiety;

L represents a nitroso moiety; a, b, d and e are numbers which together provide the electroneutrality of the general formula, whereby a is a number from 1-5; 25

b is 4, 5 or 6;

c is 0, 1 or 2; the sum of b and c being 6;

d is a number from 1-3; and e is a number from 0-2.

3. Process according to claim 2, wherein M^1 represents Mg, Zn or Co(II); M^2 represents Co(III) or Fe(III), whereby 30

a is 1, 2 or 3;

b is 5 or 6;

c is 0 or 1;

d is 1 or 2; and e is 0 or 1. 35

4. Process according to claim 3, wherein M^2 represents Co(III).

5. Process according to any of the preceding claims, wherein the metal complexes comprise up to 20 water molecules per M^2 -moiety.

6. Process according to claim 4 or 5, wherein use is made of magnesium hexacyano cobaltate. 40

7. Process according to claim 6, wherein the magnesium hexacyano cobaltate has been dehydrated at a temperature in the range of from 100 to 200 °C, in particular of from 110 to 160 °C.

8. Process according to claim 4 or 5, wherein use is made of zinc hydroxy hexacyano cobaltate.

9. Process according to claim 8, wherein the zinc hydroxy hexacyano cobaltate has been dehydrated at a temperature in the range of from 0 to 150 °C. 45

10. Process according to any of the preceding claims, wherein use is made of metal complexes having of from 0 to 50 % vacancies in their crystal lattice, based on the total number of cationic positions in the unit cell of a crystal lattice.

11. Process according to claim 10, wherein use is made of metal complexes with intra-crystalline channels having a width of from 0.2 to 0.8 nm, and preferably of from 0.3 to 0.6 nm. 50

12. Process according to any of the preceding claims, wherein use is made of metal complexes comprising particles having a diameter of from 0.1 to 30 nm.

13. Process according to any of the preceding claims, wherein a carbon dioxide comprising methane comprising feed stream is purified.

14. Process according to any of the preceding claims, which is carried out at a temperature between the condensation temperature of a gaseous feed stream and the decomposition temperature of the adsorbent. 55

15. Process according to claim 14, which is carried out at a temperature of from -70 °C to 300 °C and a total pressure of from 1 to 200 bar.

16. Process according to any of the preceding claims, which is carried out in a pressure swing type operation. 60

17. Process according to claim 16, wherein at least two beds comprising metal complexes are applied of which at least one bed is in the absorbing phase and at least one other bed is in the desorbing phase of a process cycle.

18. Process according to claim 16 or 17, wherein at least three beds comprising metal complexes are applied of which during a process cycle at least one bed is in the purging phase. 65

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19. Process according to any of the preceding claims, substantially as hereinbefore described with reference to the Example.
20. Alkanes comprising gases whenever purified by a process as claimed in any of the preceding claims.