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602/DEL/2009 27 March 2009 (27.03.2009) IN(71) Applicants (for all designated States except US): **COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH** [IN/IN]; [An Indian Registered body incorporated under, the Registration of Societies Act (Act XXXI of 1860)], Anusandhan Bhawan, 2, Rafi Marg, New Delhi 110 001 (IN). **NTPC LTD** [IN/IN]; NTPC Bhawan, Core -7, Scope Complex, Institutional Area, Lodi Road, New Delhi 110 003 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **JASRA, Raksh, Vir** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat (IN). **SOMANI, Rajesh, Shantilal** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat (IN). **TYAGI, Beena** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat (IN). **PETER, Sunil, Adavanal** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat (IN). **PILLAI, Renjith, Sasimohanan** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat (IN). **SHARMA, Ulka** [IN/IN]; Central Salt & Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002,Gujarat (IN). **HIRANI, Prakash, Dulhadinomal** [IN/IN]; Energy Technologies, NTPC Ltd, Plot no. 3, Block - E, Eco. Tech - II Udyog Vihar, Greater Noida 201 306 UP (IN). **MUKHOPADHYAY, Rabishanker** [IN/—]; Energy Technologies, NTPC Ltd, Plot no. 3, Block - E, Eco. Tech - II Udyog Vihar, Greater Noida 201 306 UP (IN).(74) Agent: **LALL, Amar, Raj**; Lall Lahiri & Salhotra, Plot No. B-28, Sector 32, Institutional Area, Gurgaon 122 001 Haryana (IN).

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(54) Title: A PROCESS FOR THE PREPARATION OF MOLECULAR SIEVE ADSORBENT FOR THE SIZE/SHAPE SELECTIVE ADSORPTION OF CARBON DIOXIDE FROM ITS GASEOUS MIXTURE WITH NITROGEN

(57) Abstract: A process for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, especially, such as in the flue gas at ambient to elevated temperature with an adsorbent comprising A-type zeolite either pore engineered by the treatment of tetra alkyl alkoxide or exchanged with potassium ions up to a desired degree of total exchangeable sodium ions to preferentially adsorb carbon dioxide. The pore engineered adsorbent contain unit cell composition  $\text{Na}_{12}[(\text{Al}_2\text{O}_2)_{12}(\text{SiO}_2)_{12-x}] 27 \text{ H}_2\text{O}$  where the value of 'x' varies from 0.001 to 1.0 and potassium exchanged adsorbent must contain at least 15% to 50% potassium ions exchanged with sodium ions present in A-type zeolite. The carbon dioxide is thereafter removed from the adsorbent by pressure swing or applying vacuum or by heating the adsorbent above the adsorption temperature and recovering the carbon dioxide as a product stream.

**“A process for the preparation of molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen”**

## **FIELD OF INVENTION**

This invention relates to a process for the preparation of molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, at ambient to elevated temperature. More specifically, the present invention provides a process for the preparation of a molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen especially from the flue gas; such an adsorbent is prepared by the surface modification of a zeolite either by simple ion exchange process or by liquid phase alkoxide deposition at external surface of the zeolite.

## **BACKGROUND OF THE INVENTION**

The contribution of CO<sub>2</sub> towards global warming is one of the most important contemporary environmental issues and it is necessary to have available technology which minimizes the discharge of CO<sub>2</sub> into the atmosphere. Increasing concentrations of carbon dioxide and other gases like methane (CH<sub>4</sub>), nitrous oxide (N<sub>2</sub>O) etc., in the earth's atmosphere are aggravating the natural greenhouse gas effect and leading to unwanted climate change, with consequent risks of extreme weather, rising sea level and adverse effects on agriculture and biodiversity. An agreement on global warming was reached by the United Nations Conference on Climate Change in Kyoto, Japan in 1997, which is known as *Kyoto Protocol*. Under this protocol, industrialized countries and those in transition to a market economy have agreed to limit or reduce their emissions of these greenhouse gases by at least 5% below 1990 levels during the period 2008 to 2012 (Kyoto Protocol To The United Nations Framework Convention On Climate Change, 1997, Available on web at: <http://unfccc.int/resource/docs/convkp/kpeng.html>). The global

warming potential (GWP) of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  are much higher than that of  $\text{CO}_2$ , but  $\text{CO}_2$  makes greatest contribution to greenhouse gas effect due to large amount of  $\text{CO}_2$  emitted to the atmosphere by human activity (IEA Greenhouse Gas R&D Programme, 1999, "Greenhouse Gases", Available on web at: <http://www.ieagreen.org.uk/climate.html>). Approximately one third of all  $\text{CO}_2$  emissions due to human activity come from the fossil fuels used for generating electricity, with each power plant capable of emitting several million tones of  $\text{CO}_2$  annually. These fossil fuels provides >80 % energy needs all over the world and will continue to do so for the foreseeable future. Typical  $\text{CO}_2$  emission from coal fired power plant is 800 kg  $\text{CO}_2$ /MWh of electricity produced (IEA Greenhouse Gas R&D Programme, 2003, "Greenhouse gas emissions from power stations", Available on web at <http://www.ieagreen.org.uk/emis4.htm>). A variety of other industrial processes also emit large amounts of  $\text{CO}_2$  from each plant, for example oil refineries, cement works, and iron and steel production. These emissions could be reduced substantially, without major changes to the basic process, by capturing and storing the emitted  $\text{CO}_2$ . Typically, flue gas from a coal fired thermal power plant contains around 15%  $\text{CO}_2$ , 81 %  $\text{N}_2$  and the rest contains other gases such as oxygen,  $\text{SO}_x$ ,  $\text{NO}_x$ , etc. on dry basis. The flue gas from a natural gas fired thermal power plant contains around 4%  $\text{CO}_2$ , 81%  $\text{N}_2$  and around 15%  $\text{O}_2$  and some minor quantities of  $\text{SO}_x$ ,  $\text{NO}_x$ , etc. on dry basis. The ultimate objective of the  $\text{CO}_2$  capture is the stabilization of greenhouse gas concentrations in the atmosphere at a level that prevents dangerous anthropogenic interference with the climate system.

Carbon dioxide present in any gas stream can be removed either by chemically absorbing in a solution of an alkali or amine, or by physically adsorbing on an adsorbent such as activated carbon or zeolite. The methods of physical adsorption of carbon dioxide using a zeolite adsorbent include a pressure swing adsorption (PSA) process, pressure temperature swing (PTSA) process, or vacuum swing adsorption (VSA) process. In these methods, adsorption of carbon dioxide by a zeolite adsorbent is effected at high pressure

and low temperature and desorption thereof from the zeolite is effected at lower pressure and/or at a higher temperature than the adsorption conditions. Upon desorption, the zeolite may be purged with a gas which is less adsorbed than carbon dioxide.

Reference may be made to U. S. Pat. No. 2,882,244, (Milton et al., 1959) wherein they claim a variety of crystalline aluminosilicates useful for CO<sub>2</sub> adsorption.

Reference may be made to U. S. Pat. No. 3,078,639, (Milton et al., 1963) which discloses a zeolite-X useful for the adsorption of carbon dioxide from a gas stream.

Reference may be made to British Patent Nos. 1,508,928, (Mobil Oil) and 1,051,621, (Furtig et al., 1913) wherein they disclose faujasite-type zeolites having silica to alumina ratio from 1.8 to 2.2. However, the adsorption capacity for carbon dioxide of these adsorbents is quite interesting but there should be a limitation because these molecular sieves are hydrophilic in nature. To increase carbon dioxide adsorption capacity, several adsorbents have been proposed based on various cation exchanged forms of zeolite molecular sieves.

Reference may be made to U. S. Pat. No. 3,885,927 (Sherman et al., 1975) wherein they claim barium cation forms of zeolite X in which 90-95% of the Na<sup>+</sup> ions are replaced by Ba<sup>2+</sup> ions.

Reference may be made to U.S. Pat. No. 4,775,396, (Rastelli et al., 1988) wherein they claim carbon dioxide removal by use of zinc, rare earth metals, a proton and ammonium cation exchanged forms of synthetic faujasite having silica to alumina ratio in broad range of 2-100.

Reference may be made to U. S. Pat. No. 3,981,698 (Leppard et al., 1976), U. S. Pat. No. 4,039,620 (Netteland, et al. 1977), U. S. Pat. No. 4,711,645 (Kumar, 1987), U. S. Pat. No. 4,986,835 (Uno et al., 1991) wherein they describe a process for separating and recovering a high purity carbonic acid gas (CO<sub>2</sub>) from a wet mixed gas containing

carbonic acid gas according to a pressure swing adsorption and separation method providing the amount of carbonic acid gas in a feeding raw material gas at least 8% by volume;

Reference may be made to U. S. Pat. No. 5,156,657 (Jain et al. 1992) wherein they claim a pressure swing absorption process for the removal from air of gaseous impurities consisting of water vapor and carbon dioxide using 13X zeolite. Though the subject process is efficient for adsorptive bed regeneration, the adsorption capacity for carbon dioxide and / or nitrogen is not reported.

Reference may be made to U. S. Pat. No. 5,531,808 (Ojo et. al., 1996) wherein they disclose a method of removing carbon dioxide from a gas stream by using a zeolite adsorbent, wherein the gas stream is contacted with a type X zeolite having a silicon/aluminum atomic-ratio of about 1.0 to 1.15 and having been ion-exchanged with a cation selected from the ions of groups 1A, 2A, 3A, 3B, the lanthanide series of the periodic table and mixtures thereof at a temperature of about -50° C to about +80° C. It is noted that the change of the uptake of carbon dioxide depending upon the pressure of carbon dioxide is examined, but, the selective adsorption of carbon dioxide in a gaseous mixture containing carbon dioxide and nitrogen is not examined therein. It is shown that Li-LSX, Ca-LSX is superior to Na-LSX in the uptake of carbon dioxide, but, the adsorption selectivity between carbon dioxide and nitrogen is not studied.

Reference may be made to U.S. Pat. No.5,914,455 (Jain et al., 1999) wherein they claim a method of removing water vapor and carbon dioxide from a gas wherein water vapor is first removed and then carbon dioxide is removed by using sodium LSX zeolite as adsorbent has been proposed. However, this patent is silent on the removal of carbon dioxide from a gaseous mixture containing carbon dioxide and nitrogen.

Reference may be made to U. S. Pat. No. 6,616,732 (Grandmougin et al., 2003) which discloses a novel family of zeolite adsorbents, suited to the decarbonation of gas flows

contaminated by CO<sub>2</sub>, comprising a mixture of zeolite X and zeolite LSX, these adsorbents being predominantly exchanged with sodium or with strontium. The process for producing an agglomerated adsorbent as defined in this patent, comprising several steps such as agglomerating and shaping, drying at low temperature and activating at a temperature of between 300 and 700° C, optional zeolitization of the binder, washing, drying and activating the product obtained. It does not disclose the adsorption selectivity between carbon dioxide and nitrogen and also does not provide the breakthrough data of carbon dioxide and nitrogen ad/desorption.

Reference may be made to U. S. Pat. No. 6,530,975 (Rode et al., 2003) wherein they claim preparation of a molecular sieve adsorbent for the purification of gas streams containing water vapor and carbon dioxide. The adsorbent is a combination of sodium form of a low-silica faujasite, having a residual content of potassium ions less than about 8.0 percent (equiv.), a low content of crystalline and amorphous admixtures and crystal sizes generally within the range of 1- 4 µm, and a binder. The process for the adsorbent preparation comprises of low silica faujasite synthesis, sodium-potassium ion exchange, blending and granulation. It provides the carbon dioxide adsorption isotherms for low-silica faujasite having differing percentages of residual potassium cations and compares the carbon dioxide adsorption of various adsorbents including the molecular sieve 5A (CaA-94.5 % Ca<sup>2+</sup>), molecular sieve 10A (CaX), molecular sieve 13X (NaX) and calcium low-silica faujasite with a potassium ion content of 0.16 percent. However, it does not disclose adsorption data for carbon dioxide from its mixture with nitrogen.

Reference may be made to U. S. Pat. No. 6,537,348 (Hirano et al., 2003) wherein they claim a method of adsorptive separation of carbon dioxide from a gaseous mixture comprising carbon dioxide and gases less polar than carbon dioxide comprising contacting the gaseous mixture with a zeolite adsorbent is effected wherein carbon dioxide present in

the gaseous mixture as contacted with the zeolite has a partial pressure of 0.1 to 50 mmHg, and the zeolite adsorbent is a shaped product comprised of at least 95%, as determined in the basis of the moisture equilibrium adsorption value, of a low-silica type X zeolite having an  $\text{SiO}_2 / \text{Al}_2\text{O}_3$  molar ratio of 1.9 to 2.1. Preferably, the zeolite adsorbent is ion-exchanged with lithium and/or sodium, and is prepared by a process including a step of contacting with a caustic solution a calcined product of a mixture of a low-silica type X zeolite and kaolin clay whereby the kaolin clay is converted to a low-silica type X zeolite. The method of the present invention is claimed to be employed for purification of air when cryogenic separation of air is conducted, or for purification of natural gas. However, this patent does not disclose adsorption data for adsorptive separation of carbon dioxide from a gaseous mixture wherein carbon dioxide content is higher; about 10 -15%, as in flue gas from power plant.

Reference may be made to U. S. Pat. No. 7,011,695 (Moreau et al., 2006) wherein they disclose zeolite adsorbent, and method of production, exchanged with calcium and barium cations, for purifying or separating a gas or gas mixture, in particular air, so as to remove there from the impurities found therein, such as hydrocarbons and nitrogen oxides. The adsorbent is preferably an X or LSX zeolite and the gas purification process is of the temperature swing adsorption type. This patent does not disclose sorption data for carbon dioxide and nitrogen.

All of these molecular sieve adsorbents are characterized by carbon dioxide adsorption capacity extended at moderate and high partial pressures of the admixture to be adsorbed. However, their capacity to adsorb at low partial pressure of  $\text{CO}_2$  (< 5 Torr) and at ambient temperatures is not sufficient to provide the purity of the gas required. In addition, due to the relatively short time before  $\text{CO}_2$  breakthrough, the water adsorption capacity of these adsorbents appears to be only 10-15 percent of their potential. This decreases adsorbent performance in such applications as TSA and PSA air pre-purification units where carbon dioxide inlet adsorption is very low.

Reference may be made to U.S Pat. No. 6,379,430 (Monereau et al., 2002) wherein they claim activated alumina having specific surface area as an adsorbent for removing CO<sub>2</sub> and/or H<sub>2</sub>O present in a gas stream, which also claims that these adsorbents are more efficient than the conventional alumina adsorbents for gas purification. However, this invention does not disclose capability of removing CO<sub>2</sub> and / or N<sub>2</sub> present in a gas stream.

Reference may be made to U. S. Pat. No. 5,917,136 (Gaffeney et al., 1999) wherein they claim a pressure swing adsorption process for absorbing CO<sub>2</sub> from a gaseous mixture containing CO<sub>2</sub> by introducing the gaseous mixture at a first pressure into a reactor containing a modified alumina adsorbent maintained at a temperature ranging from 100 °C and 500 °C to adsorb CO<sub>2</sub> to provide a CO<sub>2</sub> laden alumina adsorbent and a CO<sub>2</sub> depleted gaseous mixture and the CO<sub>2</sub> laden alumina adsorbent is regenerated by purging with a weakly adsorbing gas at lower pressure. However, this process needs very high temperature for the CO<sub>2</sub> adsorption.

Reference may be made to U. S. Pat. No. 7,314,847 (Siriwardane, 2008) wherein they claim a process for making granular sorbent to capture carbon dioxide from gas streams comprising homogeneously mixed metal oxides and a binder comprising of sodium ortho-silicate, calcium sulfate dehydrate, alkali silicates, calcium aluminate, bentonite, inorganic clays and organic clays. However, it does not disclose equilibrium sorption data for carbon dioxide and nitrogen.

Reference may be made to U. S. Pat. No. 6,878,657 (Jasra et al., 2005) wherein they claim the use of pore mouth control of zeolite NaA with liquid phase alkoxide deposition on the external surface at ambient conditions of temperature and pressure, for developing a novel molecular sieve adsorbent for the separation and purification of gaseous mixtures by the size/shape selective adsorption. According to their invention, the said adsorbent is useful for the separation and purification of nitrogen and argon from its mixture with

oxygen. However, it does not disclose the separation of carbon dioxide and nitrogen.

In another approach, chemical vapor deposition technique was used for controlling the pore opening size of the zeolites by the deposition of silicon alkoxide (Niwa et al., JCS Faraday Trans. I, 1984, 80, 3135-3145; Niwa et al., J. Phys. Chem., 1986, 90, 6233-6237; Ohayon et al., Applied Catalysis A- General, 2001, 217, 241-251). Chemical vapor deposition is carried out by taking a requisite quantity of zeolite in a glass reactor, which is thermally activated at 723 K in situ under an inert gas like nitrogen flow. The vapors of silicon alkoxide are continuously injected into inert gas stream, which carries the vapors to zeolite surface where alkoxide reacts chemically with silanol groups of the zeolite. Once the desired quantity of alkoxide is deposited on the zeolite, the sample is heated to 823 K in air for 4-6 hrs after which it is brought down to ambient temperature and used for adsorption. The disadvantages of the chemical vapor deposition are, (i) non-uniform coating of alkoxide which leads to the non-uniform closure of the pore mouth of zeolite, (ii) the process has to be carried out at higher temperature in order to vaporize the alkoxide, (iii) the deposition of the alkoxide requires to be done at a slow rate for better diffusion and (iv) the method is expensive and a commercial level at higher scale will be difficult.

All these inventions discuss about the equilibrium adsorption of carbon dioxide from its gaseous mixture on a particular adsorbent and none of them mention about the adsorption mechanism based on size/shape selective adsorption of carbon dioxide, since the kinetic diameter of carbon dioxide molecule (3.3 Å) is smaller than that of nitrogen molecule (3.64 Å).

The present invention provides a process for the preparation of a molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its mixture with nitrogen by the modification of the pore mouth opening of the zeolite- A adsorbent.

The novelty of the present invention lies in adjusting the desired surface properties of

zeolite based adsorbents by using ion exchange or liquid phase alkoxide deposition for making it suitable to selectively remove carbon dioxide from its mixture with nitrogen.

## OBJECTS OF THE INVENTION

The main object of the present invention is to provide a process for the preparation of a molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen.

Another object of the present invention is to provide a carbon dioxide size/shape selective adsorbent by the modification of the pore mouth opening of the zeolite -A adsorbent.

Another object of the present invention is to provide an adsorbent which selectively excludes larger molecules like nitrogen from its gaseous mixture with carbon dioxide during adsorption process.

Yet another object of the present invention is to modify the pore mouth opening of the zeolite A by simple ion exchange process or by liquid phase alkoxide deposition at external surface of the zeolite A for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen.

Still further object of the present invention is to use the size/shape selective adsorbent for the adsorption of carbon dioxide in a pressure swing adsorption (PSA) process, vacuum pressure swing adsorption (VPSA) process, or pressure temperature swing adsorption (PTSA) process, for the removal of carbon dioxide from its gaseous mixture, especially from flue gases.

## SUMMARY OF THE INVENTION

Accordingly, the present invention provides a process for the preparation of molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, at ambient to elevated temperature wherein the said process comprising providing A-type zeolite as an adsorbent either pore engineered by the treatment of tetra alkyl alkoxide or exchanged with potassium ions up to a desired degree of total exchangeable sodium ions to preferentially adsorb carbon dioxide to obtain a pore engineered adsorbent having unit cell composition  $\text{Na}_{12}[(\text{Al}_2\text{O}_2)_{12}(\text{SiO}_2)_{12+x}] 27\text{H}_2\text{O}$  wherein the value of 'x' varies from 0.001 to 1.0 and potassium exchanged adsorbent containing 15 to 50% potassium ions exchanged with sodium ions present in A-type zeolite, followed by removing carbon dioxide from the adsorbent by pressure swing or applying vacuum or by heating the adsorbent above the adsorption temperature and recovering the carbon dioxide as a product stream. The said gaseous mixture preferably contains carbon dioxide in the range of 10 to 20% and nitrogen in the range of 80 to 90% by volume.

In an embodiment of the present invention the tetra alkyl alkoxide used is tetra ethyl ortho silicate.

In another embodiment the pore engineering comprises following sub-steps:

- a. heating the commercially available zeolite-A in the temperature range of 623 K to 723 K to eliminate physically adsorbed water, for a period ranging from 3 to 6 hours;
- b. cooling the activated zeolite in a desiccators under vacuum in the range of  $1 \times 10^{-2}$  to  $1 \times 10^{-4}$  mm Hg;
- c. treating the cooled zeolite with tetra alkyl ortho silicate dissolved in a dry solvent, in the range of 1 to 10 volume/weight percent of tetra alkyl ortho silicate to zeolite, a specified period in the range of 4 to 8 hours under

- continuous stirring;
- d. recovering the solvent by conventional techniques for re-use; drying the treated zeolite in air in static condition at a temperature in the range of 293 K to 373 K
  - e. heating the modified zeolite in the temperature range of 673 K to 873 K for a period ranging from 3 to 8 hours,
  - f. cooling the zeolite at ambient temperature in static condition,

In another embodiment the tetra alkyl ortho silicate deposited on zeolite surface is converted into silica by calcination in air at a temperature between 773 to 923 K for 3 to 6 hrs.

In yet another embodiment the alkoxide deposited zeolite is having very high selectivity for carbon dioxide over nitrogen in the range of 314 - 36 for a partial pressure in the range of 100 - 760 mm Hg at 303 K.

In still another embodiment the potassium exchanged zeolite adsorbent completely exclude nitrogen from its gaseous mixture with carbon dioxide and shows infinite equilibrium selectivity for carbon dioxide over nitrogen.

In another embodiment the adsorption temperatures are in the range of 298 - 353 K.

In still another embodiment the said size/shape selective adsorbent for the selective adsorption of carbon dioxide from its gaseous mixture with nitrogen especially from the flue gas, can be used in a vacuum swing adsorption process; pressure swing adsorption process; pressure vacuum swing adsorption process; or pressure temperature swing adsorption process.

In still another embodiment the present invention is the size selective exclusion of

nitrogen from its gaseous mixture with carbon dioxide during adsorption process.

In still another embodiment of the present invention shaped products were also subjected to the dynamic adsorption studies in an adsorption breakthrough setup.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram of equilibrium adsorption isotherms of carbon dioxide and nitrogen at 303 K, in the adsorbent described in Example - 1.

FIG. 2 is a diagram of equilibrium adsorption isotherms of carbon dioxide and nitrogen at 303 K, in the adsorbent described in Example - 9.

FIG. 3 is a diagram of breakthrough curve of carbon dioxide in the adsorbent described in Example - 11 at 303 K.

FIG. 4 is a diagram of breakthrough curve of carbon dioxide in the adsorbent described in Example - 12 at 303 K.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for the preparation of a molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen especially from the flue gas at ambient to elevated temperature. Zeolites, which are microporous crystalline aluminosilicates, are finding increased applications for the separation of mixtures of compounds having closely related molecular properties. In a zeolite framework,  $\text{SiO}_2$  and  $\text{AlO}_2$  tetrahedra are connected by sharing oxygen atoms.  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions are buried in the tetrahedra of oxygen atoms and are not directly exposed to adsorbate molecules. Thus, the main interactions of the adsorbate molecules in a zeolite structure are through lattice oxygen atoms and extra framework cations. The attributes which makes zeolites attractive for separation include, an

unusually high thermal and hydrothermal stability, uniform pore structure, easy pore aperture modification and substantial adsorption capacity even at low adsorbate pressures. Furthermore, zeolites can be produced synthetically under relatively moderate hydrothermal conditions.

For the preparation of ion exchanged adsorbent sample for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, a known amount of zeolite NaA powder is treated with an aqueous solution of potassium salt at 353 K for 2-4 hrs. The amount of the potassium salt was taken in such manner that the concentration of  $K^+$  ions in the aqueous solution was theoretical equivalent of the particular value for the percentage exchange of sodium ions present in NaA. For example, for 20% theoretical exchange of sodium ions in NaA, the amount of  $K^+$  ions in the potassium salt taken was contained just equivalent for this 20% of sodium ions. The cation exchanged samples were filtered, washed and dried in a hot air oven at 353 K for overnight, and the samples were named as KA-20 and KA-30 for 20% and 30% of the sodium ions theoretically exchanged with potassium ions. Carbon dioxide and nitrogen equilibrium adsorption studies in these samples were carried out at 303 K and 333 K in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010), after activating the sample at 623 K under vacuum for about 4 - 8 hrs as described in the examples herein. During analysis, the samples were evacuated completely and requisite amount of the adsorbate gas was injected into the volumetric set up at volumes required to achieve a targeted set of pressures ranging from 0.1 to 850mmHg. A minimum equilibrium interval of 5 seconds with a relative target tolerance of 5.0% of the targeted pressure and an absolute target tolerance of 5.000 mmHg were used to determine equilibrium for each measurement point. Adsorption temperature was maintained ( $\pm 0.1K$ ) by circulating water from a constant temperature bath (Julabo F25, Germany).

For the preparation of liquid phase alkoxide deposited adsorbent samples, zeolite NaA powder was used as the starting material. A known amount of zeolite NaA powder was

activated at 673 K under an inert atmosphere in order to remove the adsorbed water and then it was cooled to room temperature. This activated zeolite sample was treated with a solution having known amount of tetra alkyl ortho silicate in a dry solvent at a solid to liquid ratio of 1:10 for 4-8 hrs at room temperature, the sample was filtered, dried and the tetra alkyl ortho silicate species deposited on the zeolite surface was converted into silica by calcination of zeolite at 823 K. The sample was named as NaA-10(TEOS) which means that 10 volume/weight percentage of tetra ethyl ortho silicate is treated with zeolite NaA sample. Carbon dioxide and nitrogen equilibrium adsorption studies in these samples were carried out at 303 K and 333 K in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010), after activating the sample at 623 K under vacuum for about 4 - 8 hrs as described in the examples herein. During analysis, the samples were evacuated completely and requisite amount of the adsorbate gas was injected into the volumetric set up at volumes required to achieve a targeted set of pressures ranging from 0.1 to 850mmHg. A minimum equilibrium interval of 5 seconds with a relative target tolerance of 5.0% of the targeted pressure and an absolute target tolerance of 5.000 mmHg were used to determine equilibrium for each measurement point. Adsorption temperature was maintained ( $\pm 0.1$ K) by circulating water from a constant temperature bath (Julabo F25, Germany).

The pure component selectivity of two gases A and B was calculated by using the equation,

$$\alpha_{A/B} = \left[ \frac{V_A}{V_B} \right]_{P,T}$$

Where,  $V_A$  and  $V_B$  are the volumes of gas A and B respectively adsorbed at any given pressure P and temperature T.

Isosteric heats of adsorption were calculated from the adsorption data collected at 288 K and 303 K using Clausius-Clapeyron equation.

$$-\Delta_{ad}H^{\circ} = R \left[ \frac{\partial \ln P}{\partial (1/T)} \right]_{\theta}$$

Where, R is the universal gas constant,  $\theta$  is the fraction of the adsorbed sites at a pressure P and temperature T.

Another important embodiment of present invention is the dynamic adsorption data of carbon dioxide from its gaseous mixture with nitrogen in the carbon dioxide selective adsorbent. For the dynamic adsorption measurements, potassium exchanged samples at particular cation exchange levels are prepared by treating the NaA spherical granules with an aqueous solution of potassium salt sufficient for the particular percent exchange of sodium ions in NaA granules with potassium ions. Liquid phase alkoxide deposited samples were shaped into 3 mm extrudate pellets for the dynamic adsorption studies. To make 100 parts by weight of NaA-10(TEOS) adsorbent pellets, 80 parts by weight of NaA-10(TEOS) powder and 20 parts by weight of bentonite clay were incorporated and mixed together for 15 minutes and then a required amount of water was added, followed by kneading for 1.5 hours. The kneaded product was extruded by using a hand-operated, extrusion machine to give a shaped product in the form of extrudates having an average diameter of 3 mm. Extrudates were dried at 80° C overnight and broken in to pieces of about 3 mm length manually. The dried extrudates were calcined at 873 K for 3 hours under air in a muffle furnace to give a shaped product containing zeolite NaA-10(TEOS). The adsorbent samples prepared as per the above mentioned procedure were filled in an adsorbent column having a dimension of 35 cm length and 1.9 cm diameter and activated in situ in the adsorbent column at heating rate of 2 K/min to 623 K and the temperature was maintained for 12- 24 hrs under N<sub>2</sub> flow for 8 - 24 hrs and then cooled to the breakthrough measurement temperatures, 303 K and 348 K respectively. The feed gas consist of around 15% CO<sub>2</sub> and 85% N<sub>2</sub>, in which N<sub>2</sub> acts as a carrier gas for the dynamic adsorption measurements, is passed through the adsorbent column at a flow rate of

around 120 ml/min. The feed concentration and the product concentration at the other end of adsorbent column, are measured in a GC instrument (GC-7610, Chemito Technologies Pvt. Ltd., Nasik, India) equipped with a TCD detector (TCD 866) using a Porapak packed column with  $H_2$  gas as a carrier gas at a flow rate of 40ml/min. Around 1.5 ml of the gas samples were taken in a gas tight syringe and analyzed in the GC. The concentration profile of carbon dioxide at the outlet of the adsorbent column is plotted against time and it is defined hereafter as the breakthrough curve of carbon dioxide in the particular adsorbent.

*The following examples are given by way of illustration and therefore should not construed to limit the scope of the present invention.*

#### **Example 1**

0.5 g of zeolite NaA was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 348 K. The equilibrium adsorption isotherms of carbon dioxide and nitrogen in NaA powder at 303 K are given in FIG. 1. The heats of adsorption, adsorption capacity and selectivity of  $CO_2$  and  $N_2$  in NaA are given in Table 1.

#### **Example 2**

10.0 g of zeolite NaA is treated with 0.1 molar aqueous solution of potassium chloride at 353 K with a solid to liquid ratio of 1:80 for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. The cation exchange was conducted for 4 times in order to replace the sodium ions present in the zeolite completely with potassium ions. A known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption

measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. Nitrogen gas did not adsorb and the equilibrium adsorption capacity for carbon dioxide was 6.2 cc/gram at 303 K and 1 atm.

### Example 3

10.0 g of zeolite NaA powder is treated with around 0.82 g of potassium chloride in 400 ml of distilled water, at 353 K for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. The sample is named as KA-20 and a known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. Nitrogen gas did not adsorb and the adsorbent sample is having almost infinite selectivity carbon dioxide over nitrogen. The heats of adsorption, adsorption capacity and selectivity of CO<sub>2</sub> and N<sub>2</sub> in KA-20 are given in Table 1.

### Example 4

10.0 g of zeolite NaA powder is treated with around 1.23 g of potassium chloride in 400 ml of distilled water, at 353 K for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. The sample is named as KA-30 and a known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. Nitrogen gas did not adsorb and the adsorbent sample is having almost infinite selectivity carbon dioxide over nitrogen. The heats of adsorption, adsorption capacity and selectivity of CO<sub>2</sub> and N<sub>2</sub> in KA-30 are given in Table 1.

#### Example 5

10.0 g of zeolite NaA powder is treated with around 0.41 g of potassium chloride in 400 ml of distilled water, at 353 K for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. A known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. The equilibrium adsorption capacities for nitrogen and carbon dioxide were 4.9 cc /gram and 83.6 cc /gram respectively at 303 K and 1 atm.

#### Example 6

10.0 g of zeolite NaA powder is treated with around 0.205 g of potassium chloride in 400 ml of distilled water, at 353 K for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. A known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. The equilibrium adsorption capacities for nitrogen and carbon dioxide were 6.2 cc /gram and 85.3 cc /gram respectively at 303 K and 1 atm.

#### Example 7

10 g of zeolite NaA powder was activated at 673 K under nitrogen atmosphere in order to remove the adsorbed water and then it was cooled to room temperature. This activated zeolite sample was treated with 0.25 ml of tetra ethyl ortho silicate (TEOS) in 100 ml dry toluene for 8 hrs at room temperature, the sample was filtered, dried and the tetra ethyl

ortho silicate species deposited on the zeolite surface was converted into silica by calcination of zeolite at 823 K for 5 hours. The sample is named as NaA-2.5(TEOS) and a known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. The equilibrium adsorption capacities for nitrogen and carbon dioxide were 6.8 cc /gram and 84.2 cc /gram respectively at 303 K and 1 atm.

#### Example 8

10 g of zeolite NaA powder was activated at 673 K under nitrogen atmosphere in order to remove the adsorbed water and then it was cooled to room temperature. This activated zeolite sample was treated with 0.5 ml of tetra ethyl ortho silicate (TEOS) in 100 ml dry toluene for 8 hrs at room temperature, the sample was filtered, dried and the tetra ethyl ortho silicate species deposited on the zeolite surface was converted into silica by calcination of zeolite at 823 K for 5 hours. The sample is named as NaA-5(TEOS) and a known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. The equilibrium adsorption capacities for nitrogen and carbon dioxide were 4.2 cc /gram and 81.7cc /gram respectively at 303 K and 1 atm.

#### Example 9

50 g of zeolite NaA powder was activated at 673 K under nitrogen atmosphere in order to remove the adsorbed water and then it was cooled to room temperature. This activated zeolite sample was treated with 5 ml of tetra ethyl ortho silicate (TEOS) in 500 ml dry toluene for 8 hrs at room temperature, the sample was filtered, dried and the tetra ethyl

ortho silicate species deposited on the zeolite surface was converted into silica by calcination of zeolite at 823 K for 5 hours. The sample is named as NaA-10(TEOS) and a known amount of the sample was activated at 623 K under vacuum ( $5 \times 10^{-3}$  mm Hg) for 12 hrs and then cooled to room temperature. Equilibrium adsorption measurements of pure carbon dioxide and nitrogen gases in this activated adsorbent were carried out in a static volumetric adsorption system (Micromeritics, USA, Model ASAP 2010) at 303 K and 333 K. The equilibrium adsorption isotherms of carbon dioxide and nitrogen in NaA-10(TEOS) powder at 303 K are given in FIG. 2. The heats of adsorption, adsorption capacity and selectivity of CO<sub>2</sub> and N<sub>2</sub> in NaA-10(TEOS) are given in Table 1.

#### Example 10

Around 100ml of the adsorbent NaA spherical granules were filled in an adsorbent column having a dimension of 35 cm length and 1.9 cm diameter and activated in situ in the adsorbent column at heating rate of 2 K/min to 623 K and the temperature was maintained for 24 hrs under N<sub>2</sub> flow and then cooled to the breakthrough measurement temperatures, 303 K and 348 K respectively. The feed gas consist of around 15% CO<sub>2</sub> and 85% N<sub>2</sub>, in which N<sub>2</sub> acts as a carrier gas for the dynamic adsorption measurements, is passed through the adsorbent column at a flow rate of around 120 ml/min. Desorption of CO<sub>2</sub> was carried out by passing N<sub>2</sub> at a flow rate of 102 ml/min, counter-currently to the feed flow. The column pressure was 1 atm (absolute) during adsorption and desorption. The breakthrough capacity of CO<sub>2</sub> in NaA granules were found to be 51.9 cc /gram and 32.4 cc /gram at temperatures 303 K and 348K respectively and at a total feed gas flow of around 120ml/min.

#### Example 11

100.0 g of zeolite NaA spherical granules were treated with around 8.2 g of potassium chloride in 4000 ml of distilled water, at 353 K for 4 hrs and then filtered, washed with distilled water and dried at 353 K in a hot air oven. The sample is named as KA-20(G)

and around 100ml of this adsorbent sample was filled in an adsorbent column having a dimension of 35 cm length and 1.9 cm diameter and activated in situ in the adsorbent column at heating rate of 2 K/min to 623 K and the temperature was maintained for 24 hrs under  $N_2$  flow and then cooled to the breakthrough measurement temperatures, 303 K and 348 K respectively. The feed gas consist of around 15%  $CO_2$  and 85%  $N_2$ , in which  $N_2$  acts as a carrier gas for the dynamic adsorption measurements, is passed through the adsorbent column at a flow rate of around 120 ml/min. Desorption of  $CO_2$  was carried out by passing  $N_2$  at a flow rate of 102 ml/min, counter-currently to the feed flow. The column pressure was 1 atm (absolute) during adsorption and desorption. The  $CO_2$  breakthrough in KA-20(G) granules at 303 K is shown in FIG. 3.

### Example 12

The adsorbent mentioned in Example 9 was shaped into 3 mm extrudate pellets for the dynamic adsorption studies. To make 100 parts by weight of NaA-10(TEOS) adsorbent pellets, 80 parts by weight of NaA-10(TEOS) powder and 20 parts by weight of bentonite clay were incorporated and mixed together for 15 minutes and then a required amount of water was added, followed by kneading for 1.5 hours. The kneaded product was extruded by using a hand-operated, extrusion machine to give a shaped product in the form of extrudates having an average diameter of 3 mm. Extrudates were dried at 80° C overnight and broken in to pieces of about 3 mm length manually. The dried extrudates were calcined at 873 K for 3 hours under air a muffle furnace to give a shaped product containing zeolite NaA-10(TEOS). Around 100ml of this adsorbent sample was filled in an adsorbent column having a dimension of 35 cm length and 1.9 cm diameter and activated in situ in the adsorbent column at heating rate of 2 K/min to 623 K and the temperature was maintained for 24 hrs under  $N_2$  flow for 8 - 24 hrs and then cooled to the breakthrough measurement temperatures, 303 K and 348 K respectively. The feed gas consist of around 15%  $CO_2$  and 85%  $N_2$ , in which  $N_2$  acts as a carrier gas for the dynamic adsorption measurements, is passed through the adsorbent column at a flow rate of

around 120 ml/min. Desorption of CO<sub>2</sub> was carried out by passing N<sub>2</sub> at a flow rate of 102 ml/min, counter-currently to the feed flow. The column pressure was 1 atm (absolute) during adsorption and desorption. The CO<sub>2</sub> breakthrough in NaA-10(TEOS) pellets at 303 K is shown in FIG. 4. The breakthrough capacity of CO<sub>2</sub> in NaA-10(TEOS) adsorbent pellets were found to be 44.7 ml/g and 25.0 ml/g at temperatures 303 K and 348K respectively and at a total feed gas flow of around 120ml/min.

The main advantages of the present invention are:

1. The size/shape selective adsorbent, for the selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, can be prepared simply by the ion exchange of zeolite or by the liquid phase alkoxide deposition on the external surface of the zeolite A.
2. The alkoxide deposition is uniform on the zeolite surface.
3. The equilibrium adsorption selectivity for carbon dioxide over nitrogen increases tremendously.
4. Cation exchanged zeolite A above a particular cation exchange level, showed selective exclusion of nitrogen from its gaseous mixture with carbon dioxide.

We claim:

- 1.A process for the preparation of molecular sieve adsorbent for the size/shape selective adsorption of carbon dioxide from its gaseous mixture with nitrogen, at ambient to elevated temperature wherein the said process comprising providing A type zeolite as an adsorbent either pore engineered by the treatment of tetra alkyl alkoxide or exchanged with potassium ions up to a desired degree of total exchangeable sodium ions to preferentially adsorb carbon dioxide to obtain a pore engineered adsorbent having unit cell composition  $\text{Na}_{12}[(\text{Al}_2\text{O}_2)_{12}(\text{SiO}_2)_{12-x}] \cdot 27 \text{H}_2\text{O}$  wherein the value of 'x' varies from 0.001 to 1.0 and potassium exchanged adsorbent containing 15 to 50% potassium ions exchanged with sodium ions present in A type zeolite, followed by removing carbon dioxide from the adsorbent by pressure swing or applying vacuum or by heating the adsorbent above the adsorption temperature and recovering the carbon dioxide as a product stream.
- 2.A process as claimed in claim 1, wherein the gaseous mixture used contains carbon dioxide in the range of 10 to 20% and nitrogen in the range of 80 to 90% by volume.
- 3.A process as claimed in claim 1, wherein the tetra alkyl alkoxide used is tetra ethyl ortho silicate.
- 4.A process as claimed in claim 1, wherein the pore engineering comprises following sub-steps:
  - a. heating the commercially available zeolite A in the temperature range of 623 K to 723 K to eliminate physically adsorbed water, for a period ranging from 3 to 6 hours to obtain activated zeolite;
  - b. cooling the activated zeolite of step a in a desiccators under vacuum in the range of  $1 \times 10^{-2}$  to  $1 \times 10^{-4}$  mm Hg;
  - c. treating the cooled zeolite of step b with tetra alkyl ortho silicate dissolved in a dry solvent, in the range of 1 to 10 volume/weight percent of tetra alkyl ortho

silicate to zeolite, a specified period in the range of 4 to 12 hours under continuous stirring;

- d. recovering the solvent by conventional techniques for re-use; (5) drying the treated zeolite in air in static condition at a temperature in the range of 293 K to 373 K to obtain modified zeolite;
  - e. heating the modified zeolite of step d in the temperature range of 673 K to 873 K for a period ranging from 3 to 8 hours.
  - f. cooling the zeolite of step e at ambient temperature in static condition.
5. A process as claimed in claim 1, wherein the tetra alkyl ortho silicate deposited on zeolite surface is converted into silica by calcination in air at a temperature in the range of 773 to 923 K for a time period in the range of 3 to 6 hrs.
6. A process as claimed in claim 1, wherein the alkoxide deposited zeolite is having very high selectivity for carbon dioxide over nitrogen in the range of 314 to 36 for a partial pressure in the range of 100 to 760 mm Hg at 303 K.
7. A process as claimed in claim 1, wherein the potassium exchanged zeolite adsorbent completely exclude nitrogen from its gaseous mixture with carbon dioxide and shows infinite equilibrium selectivity for carbon dioxide over nitrogen.
8. A process as claimed in claim 1, wherein the adsorption temperatures are in the range of 298 to 353 K.

Table 1 Heat of adsorption, adsorption capacity, and equilibrium selectivity of CO<sub>2</sub> and N<sub>2</sub> in pore engineered zeolite

| Adsorbent | -ΔH (kJ/mol) | Adsorption capacity at 1 atm. |                |                 |                | Selectivity at 303K               |                |                    |
|-----------|--------------|-------------------------------|----------------|-----------------|----------------|-----------------------------------|----------------|--------------------|
|           |              | (cc.g <sup>-1</sup> )         |                |                 |                | $\alpha_{\text{CO}_2/\text{N}_2}$ |                |                    |
|           |              | CO <sub>2</sub>               | N <sub>2</sub> | 303K            |                | 333K                              |                | 100mm Hg 760 mm Hg |
|           |              |                               |                | CO <sub>2</sub> | N <sub>2</sub> | CO <sub>2</sub>                   | N <sub>2</sub> |                    |
| Example 1 | 45.4         | 18.7                          |                | 88.0            | 7.5            | 74.2                              | 2.0            | 64 12              |
| Example 3 | 37.5         | -                             |                | 80.3            | Nil            | 52.8                              | Nil            | ∞ ∞                |
| Example 4 | 37.8         | -                             |                | 71.9            | Nil            | 44.2                              | Nil            | ∞ ∞                |
| Example 9 | 32.5         | 22.4                          |                | 78.6            | 2.2            | 64.7                              | 0.6            | 314 36             |

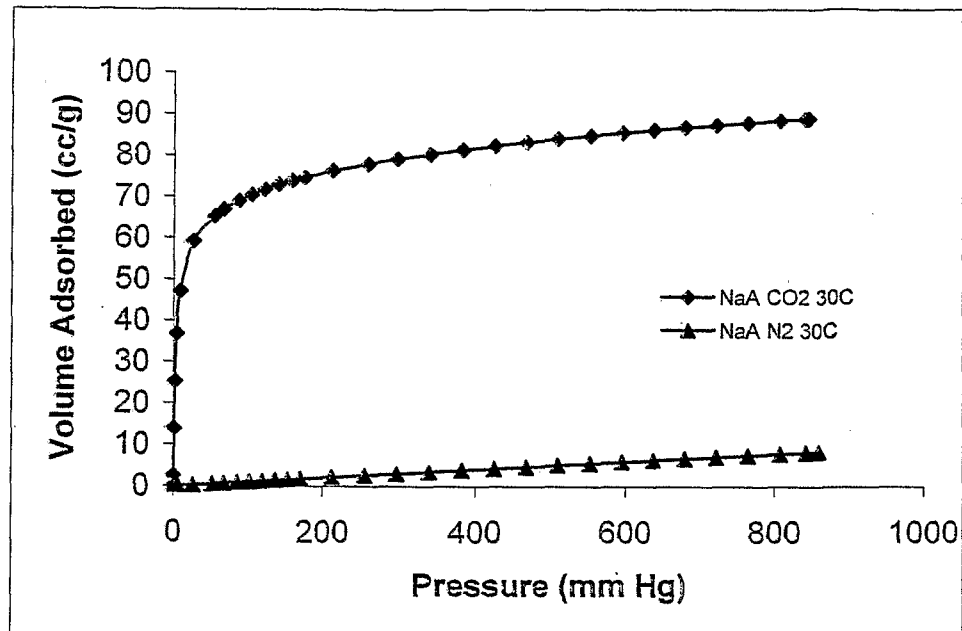


FIG. 1 Equilibrium adsorption isotherms of carbon dioxide and nitrogen at 303 K, in the adsorbent described in Example - 1.

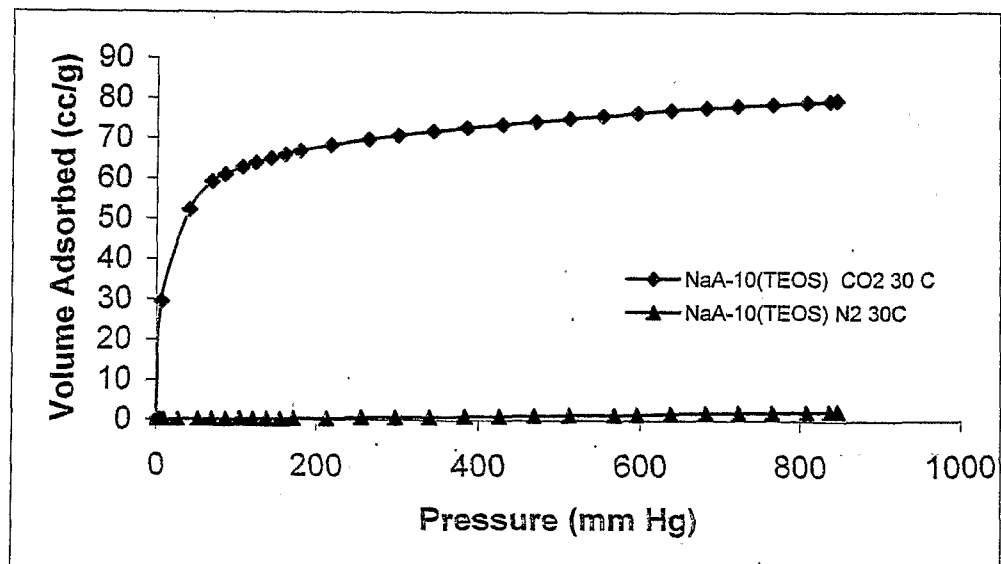


FIG. 2 Equilibrium adsorption isotherms of carbon dioxide and nitrogen at 303 K, in the adsorbent described in Example - 9.

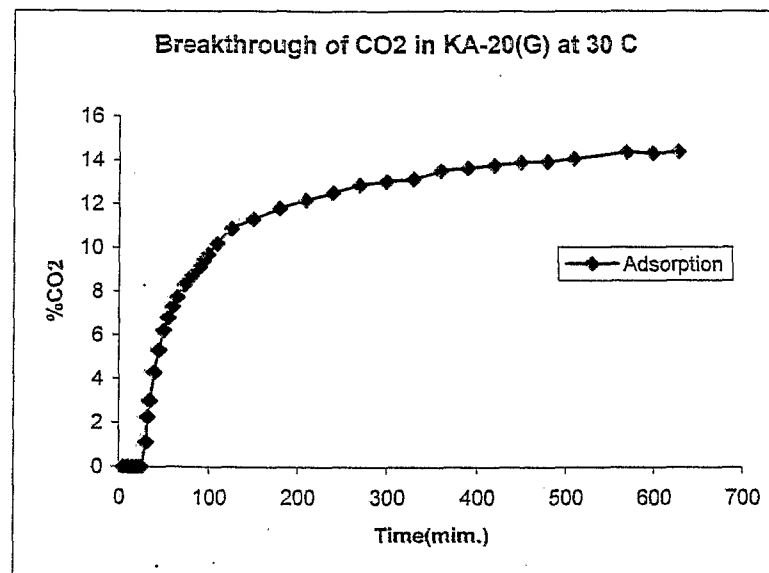


FIG. 3 Breakthrough curve of carbon dioxide in the adsorbent described in Example - 11 at 303 K.

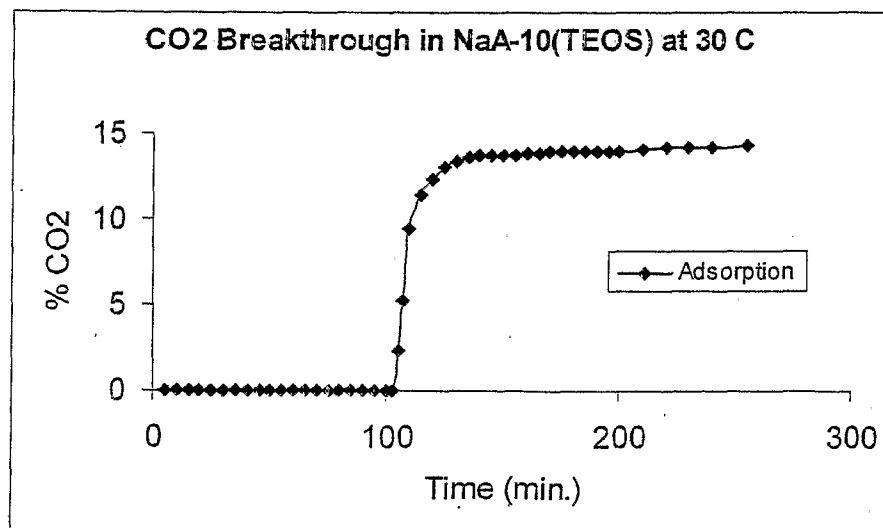


FIG. 4 Breakthrough curve of carbon dioxide in the adsorbent described in Example - 12 at 303 K.