DESCRIPTION

ADHESIVE, PROCESS FOR PREPARING THE SAME, AND METHOD FOR RECOVERING VAPOR OF HYDROCARBON BY UTILIZING CONDENSATION BY COOLING

TECHNICAL FIELD

The present invention relates to adsorbents for the gases of volatile organic compounds (hereinafter referred to as "VOC") and processes for preparing the same. More particularly, the present invention relates to adsorbents optimal for use as adsorbents for recovering VOC gases by a pressure swing adsorption (hereinafter referred to as "PSA") process, and to processes for preparing the same. The adsorbents for VOC gases of the present invention are especially suitable for use as adsorbents for recovering VOC gases contained in the air in gas stations, oil tank stations, and the like by a PSA process.

The present invention further relates to an adsorptive method for recovering a gaseous hydrocarbon from, for example, a waste gas containing the hydrocarbon and the like, by which the hydrocarbon is easily and efficiently recovered using cooling condensation.

BACKGROUND ART

Gasolines, organic solvents for coating, chlorinated organic solvents for cleaning, and the like contain a large amount of liquid organic compounds having a high vapor pressure. Since these compounds have the property of readily volatilizing, they are called volatile organic compounds (hereinafter referred to simply as "VOC"). At present, VOCs are used in large amounts in various fields including coating, printing, and cleaning besides in fuels for transportation, such as gasolines and the like, and VOC vapors are volatilizing therefrom and diffusing into the air.

Upon irradiation with ultraviolet, VOCs present in air even in low concentrations react with oxygen to yield oxidants (general name for oxidizing substances including ozone and peroxides) causative of photochemical smog. Furthermore, the ozone generated reacts with nitrogen oxides (NO_x), sulfur oxides (SO_x), and the like to yield nitric acid and sulfuric acid, which are causative of acid rain.

Thus, influences of VOCs present even in relatively low concentrations, not to mention VOCs present in high concentrations, on the atmospheric environment have become not negligible. The emission of VOCs into the air is severely restricted especially in

Europe and America, where health problems posed by photochemical smog, the destruction of forests caused by acid rain, and the like are serious. In Japan also, local self-governing bodies having an industrial district where air pollution is serious have begun to control the emission by means of local regulations. It is thought that in the future, the control will be tightened and the control areas will expand.

Virtually, however, people have little interest in VOCs because much attention has not been focused on influences of VOCs on the atmospheric environment. Almost no techniques for recovering VOCs have therefore been developed.

The only conventional technique for VOC recovery may be combustion apparatuses such as apparatuses for catalyzed combustion which are installed in coating plants of automobile manufacturers, large-scale printing plants of major printing companies, and the like from the standpoints of improving the working environment in the plants, preventing the emission of offensive odors into the neighborhood thereof, *etc.* However, these apparatuses are used only when a VOC-containing waste gas generates in a large amount. It is therefore impractical, from the standpoint of preserving the

atmospheric environment, to employ such a combustion apparatus in general places of business.

On the other hand, there is a strong desire for the development of a practical technique for recovering VOCs emitted into the air from small-scale general VOC emission sources, such as gas stations, fuel oil shipping facilities, oil tank stations, the cleaning industry, the coating industry, and the like, so as to promote preservation of the atmospheric environment.

Under these circumstances, a recovery apparatus based on pressure swing adsorptive separation (PSA) is attracting attention as a process suitable for VOC recovery because it can be small and the operation and maintenance thereof are easy. In order to maximize the performance of a PSA process, the recovery apparatus should be packed with an adsorbent suitable for the substance to be recovered. However, the problem for the apparatus is that there currently is no high-performance adsorbent for PSA which is suitable for VOC recovery.

In addition, the gases containing VOCs to be recovered which are being emitted from general VOC emission sources, such as gas stations, oil tank stations, fuel oil shipping facilities, and the like, vary in their emission amounts with time and fluctuate in the concentrations therein of VOCs to be recovered.

Consequently, it is also important to take account of these factors for efficiently recovering VOCs by a PSA process.

Also, in a PSA process, the performance of an adsorbent is directly related to the ability to recover a VOC, and the adsorbent cost accounts for a large proportion of the process cost. Although an inexpensive and high-performance adsorbent is hence required, the conventionally known adsorbents for general organic gases or for dehydration, such as active carbons, zeolites, silica, silica gels, and the like, are unsuitable for use as adsorbents for the PSA of VOCs, as will be described below in order.

VOC molecules which are more apt to be emitted into the air, namely which have higher vapor pressures, tend to have smaller molecular sizes. Such molecules are thought to undergo capillary condensation in small pores of an adsorbent and be thus relatively easily adsorbed.

Active carbons not only have advantages in adsorbing ability that they have a specific surface area as large as 1000 m^2/g or larger and micropores, but have excellent moisture resistance. However, a fear in safety has been pointed out because air and VOC molecules come into contact with active carbons, which

are a combustible substance. It is hence impractical in Japan to use active carbons in VOC recovery apparatuses.

Namely, for eliminating the above problem concerning safety, an adsorbent is necessary which has a large surface area and micropores and adsorbs VOC molecules in air even under saturation with water vapor, and which is an inorganic noncombustible adsorbent (hereinafter referred to as a "noncombustible adsorbent").

Active carbons, which are a representative adsorbent, have a specific surface area 1000 m^2/g or more and are an optimal adsorbent for VOCs when judged based on their adsorbing ability only.

However, because of the combustibility of active carbons, it is difficult, from the standpoint of safety control, to use the same as an adsorbent in a VOC adsorber based on a PSA process in VOC-emitting places such as gas stations, where combustible gases are handled, or oil tank stations.

Inorganic oxide adsorbents, such as zeolites and the like, are hence attracting attention as noncombustible adsorbents. Attempts have been made to use such an inorganic adsorbent in a pressure-and-temperature swing adsorption (hereinafter referred to as "PTSA") process, which is almost the same in adsorption

principle as the PSA process, and in a temperature swing adsorption (hereinafter referred to as "TSA") process.

These methods, in which an exceedingly common inorganic oxide adsorbent, such as a zeolite or the like, is used, involve a step in which temperature is swung in order to desorb the water which has been adsorbed onto the adsorbent together with a VOC.

However, these adsorptive separation methods are intended to be used for adsorbing a VOC present in a relatively high concentration. No report has so far been found on the practical use of any of these methods in collecting VOCs such as those emitted from gas stations, oil tank stations, or the like.

The reasons therefor are as follows. First, such VOCs are difficult to adsorb because they are present in low concentrations. Secondly, saturation with water vapor influences the adsorption of VOCs.

Although inorganic oxide adsorbents having a large surface area may be thought to efficiently adsorb low-concentration VOCs and desorb the VOCs, use of such adsorbents results in selective adsorption of water molecules only, which have a large dipole moment, and in considerably reduced adsorption and desorption of VOCs. This is because inorganic oxide adsorbents have many

highly polar groups, such as hydroxyl (OH) groups and the like, on the surface thereof.

For example, zeolites have an acidic nature and a high affinity for water because of their low silica-to-alumina ratio (SiO_2/Al_2O_3) and hence selectively adsorb water, although they have a large specific surface area.

The affinity for water poses a serious problem especially when VOCs are present in low concentrations.

Specifically, silica (silicon oxide, SiO_2) *per se* shows high water repellency. However, the surface of silica having a large surface area generally has many residual silanol (Si-OH) groups, which are hydrophilic.

Since competitive adsorption between water vapor and a VOC proceeds in a VOC adsorption step in the PSA of the VOC, use of an adsorbent on which many hydrophilic groups are present results in adsorption of a large amount of water and hence in a reduced VOC adsorption. In addition, since the adsorbent absorbs water in a large amount, it has a problem that the water infiltrates into inner parts of the adsorbent to cause cracks therein.

For eliminating residual silanol groups, use may be made of a method in which an organosilicon compound, such as methoxytrimethylsilane ($CH_3O-Si-(CH_3)_3$) or the like, is contacted with silica to couple the

organosilicon compound with the silanol groups present on the surface.

On the other hand, a high-silica zeolite (HS-zeolite) obtained by removing aluminum from a zeolite through a treatment, such as extraction with an acid or the like, without destroying the zeolite crystals to thereby hydrophobize the zeolite without impairing the excellent porosity characteristics thereof, including a large specific surface area, is attracting attention as an adsorbent for low-concentration VOCs.

Many zeolites have a surface area around 500 m^2/g, and these zeolites fall under the group of inorganic noncombustible adsorbents having relatively large surface areas. However, zeolites have a problem that because of their low silica/alumina ratio (SiO_2/Al_2O_3 ratio), they have an acidic nature attributable to alumina, have a high affinity for water, and hence selectively adsorb water present in air.

It has hence been proposed to use, for the PSA of VOCs, an adsorbent obtained by removing aluminum from a zeolite through a treatment, e.g., extraction with an acid, without destroying the crystals thereof to thereby hydrophobize the zeolite while minimizing the resultant impairment of properties thereof including specific

surface area. However, this technique is not profitable because the treatment for removing aluminum is costly.

As can be seen from the example of high-silica zeolite, silicon oxide (SiO_2) is a hydrophobic substance. Virtually, however, a silica gel (SiO_2) exceedingly highly absorbs water because hydrophilic groups (silanol groups: SiOH) are present on the surface thereof. Namely, a silica gel as it is cannot be used as an adsorbent for the PSA of VOCs.

There is a method for enhancing the hydrophobicity of a silica gel which comprises methylating the surface silanol groups to hydrophobize the silica gel. In this method, an organosilicon compound, such as methoxytrimethylsilane ($CH_3OSi(CH_3)_3$), hexamethyldisilazane ($(CH_3)_6Si_2NH$), diphenyldichlorosilane ($(C_6H_5)_2SiCl_2$), or the like, is contacted with a silica gel to couple the organosilicon compound with silanol groups present on the surface thereof and thus convert the silanol groups to $SiO\text{-}Si\text{-}R_n$ (R is an alkyl or phenyl group and n is a natural number) to thereby hydrophobize the silica gel.

Although the above method can almost completely hydrophobize a silica gel, the treatment significantly impairs properties concerning adsorbing ability, such as specific surface area. As a result, the treated silica

gel has a reduced VOC adsorption and this adsorbent should hence be packed in a larger amount. Namely, the adsorbent cost is increased rather than reduced. In addition, the organosilicon compound used as a hydrophobizing agent is expensive, and care should be taken in handling the compound because it is a harmful volatile compound. Consequently, the above method for adsorbent production also has problems concerning profitability and safety.

Also, one of especially problematic stationary sources of gaseous hydrocarbons is oil tank stations and the like where volatile hydrocarbons are landed or loaded into storage tank trucks or coasters. The waste gas which generates in the landing or loading contains hydrocarbons in a relatively high concentration of from 10 to 30%. Another problematic hydrocarbon source is coating facilities, printing facilities, and the like, where the solvents used therein emit gaseous hydrocarbons in a relatively low concentration of from several tens to several thousands ppm. Conventionally extensively used techniques for treating or recovering such a waste gas containing gaseous hydrocarbons include the absorption method using an absorbing liquid and the adsorption method both for high concentrations and the adsorption method for low concentrations. Most of the

adsorbents employed in the adsorption method are active carbons and zeolites.

Techniques for the adsorption method include the fixed bed type and the fluidized bed type from the standpoint of apparatus constitution. Of these, the fixed bed method (apparatus) for treating and recovering an effluent gas containing a gaseous hydrocarbon (solvent) include a TSA process, a PSA process, and a PTSA process which is a combination thereof; these processes are suitably used according to the kinds of solvents and the conditions for recovery. The TSA process include a wet TSA process, in which an adsorbent layer saturated with a solvent is heated by directly passing steam through the adsorbent layer to conduct desorption, and a dry TSA process, in which the adsorbent is heated by using a small amount of a heated desorbing gas to conduct adsorption/desorption without using steam for desorption. On the other hand, the PSA process is a technique in which adsorption and desorption are conducted at an elevated pressure and ordinary pressure, respectively, or conducted at ordinary pressure and a reduced pressure, respectively; in this process, the pressure dependence of the adsorption capacity of an adsorbent is utilized to conduct adsorption/desorption. Furthermore, the PTSA

process is a technique in which adsorption is conducted at ordinary temperature and ordinary pressure and desorption is conducted at an elevated temperature and a reduced pressure; this process combines features of both TSA and PSA processes. In these fluidized bed and fixed bed processes, a technique for recovering a solvent in a desorbed gas has been employed in which the solvent is recovered by means of cooling condensation with a cooling water, a 0-5°C chilling unit, or a combination thereof and the uncondensed gas is recycled to the feed gas line.

Also, apparatuses for environmental preservation, regardless of whether they are for VOC recovery or not, generally impose new cost burdens on the enterprises that introduce the apparatuses. There is hence a strong desire for an inexpensive economical process. In PSA processes, for example, the adsorbent cost accounts for a large proportion of the cost of the whole process and it is crucially important to develop an inexpensive adsorbent.

However, organosilicon compounds, such as methoxytrimethylsilane and the like, necessitate complicated facilities for coupling reactions because they are volatile. In addition, these organosilicon compounds are expensive. There has hence been a problem

that hydrophobizing treatment by the coupling method in an industrial process is not profitable. The high-silica zeolite also has a problem that the treatment for aluminum removal is costly and use thereof in an industrial process is not profitable.

As described above, none of the conventional adsorbents can efficiently collect a low-concentration VOC and is profitable and suitable for an industrial process.

There is hence a strong desire for an adsorbent which can efficiently recover a VOC, is inexpensive, and withstands long-term use, namely, a noncombustible adsorbent which has a large surface area and is less influenced by saturation with water vapor, in order to enhance the profitability of a VOC recovery apparatus based on a PSA process.

Furthermore, the conventional adsorptive recovery methods have the following problems because solvent recovery in the adsorption/desorption apparatus is after all conducted in a once-through operation. For example, when a desorbed gas is condensed by cooling at 1 atm to recover a solvent, the percentage recovery is represented by the equation: percentage recovery = (1-b/a)/(1-b) (wherein a represents the partial pressure (atm) of the hydrocarbon solvent in the desorbed gas,

and b represents the saturation vapor pressure (atm) of the hydrocarbon solvent to be recovered, as measured at a temperature difference during the cooling condensation). Consequently, no solvent is recovered when a<b, and the closer the value of a to that of b, the lower the percentage recovery. In order to heighten the percentage recovery, a measure has therefore been taken, e.g., to reduce the value of b by installing a chilling unit as stated above or to increase the value of a. Moreover, the conventional adsorptive recovery methods are unsuitable for fixed bed type adsorption processes because the concentration of a desorbed gas decreases in proportion to the decreasing concentration of a feed gas.

Accordingly, an object of the present invention is to provide adsorbents for the PSA of VOCs, which combines the high ability to reversibly adsorb VOCs and high hydrophobicity and are economical, and to provide processes for preparing the adsorbents.

Another object of the present invention is to provide an adsorptive method for recovering a gaseous hydrocarbon contained in a waste gas, in which the hydrocarbon is easily and efficiently recovered using simple equipment without necessitating facilities such as a chilling unit.

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DISCLOSURE OF THE INVENTION

Under the circumstances described above, the present inventors thought that in order to obtain an adsorbent which efficiently adsorbs VOCs and has enhanced resistance to cracking caused by water, it is necessary to remove hydrophilic groups to thereby reduce the ability to adsorb water, i.e., improve hydrophobicity, and to simultaneously enhance the ability to adsorb VOCs. The inventors repeatedly made experiments and, as a result, have found that an adsorbent consisting of a porous molded material comprising silica as the main component and having specific porosity characteristics concerning specific surface area, pore volume, average pore diameter, and the like, has excellent hydrophobicity and the excellent ability to adsorb VOCs. The present invention has thus been completed. It has further been found that such an adsorbent can be produced by a heat treatment conducted under specific conditions. The processes of the present invention have thus been completed.

In order to accomplish the above objects, the adsorbent according to the present invention comprises a porous molded material comprising silica as the main component and having a specific surface area of from 400

to 700 m^2/g, an average pore diameter of from 0.4 to 3.0 nm, and a water vapor adsorption of from 3 to 10 ml-water-vapor/g-adsorbent, and selectively adsorbs gases of volatile organic compounds having 1 to 12 carbon atoms.

The expression "selectively adsorbs gases of volatile organic compounds having 1 to 12 carbon atoms" herein means to selectively adsorb the gases of volatile organic compounds having 1 to 12 carbon atoms among gases and gaseous components other than water vapor.

Furthermore, the process for adsorbent production according to the present invention is a process for preparing an adsorbent which selectively adsorbs gases of volatile organic compounds having 1 to 12 carbon atoms, comprising:

heating molded pellets of either silica or a silica gel which have a specific surface area of 600 m^2/g or larger, a pore volume of from 0.05 to 0.5 cm^3/g, and an average pore diameter of from 0.4 to 3.0 nm to a predetermined temperature of from 550°C to 700°C at a heating rate of from 1 to 20 °C/min, and keeping the pellets at the predetermined temperature for a predetermined period of time. The adsorbent produced by this process of the present invention has a decreased

ratio in specific surface area of from 5 to 40% and has a water vapor adsorption of from 3 to 10 ml/g.

It has further been found that a highly hydrophobic adsorbent for the PSA of VOCs can be economically produced by subjecting silica or a silica gel each having specific properties to heat treatment or burning treatment while strictly controlling the temperature. It has furthermore been found that properties important for the adsorbing ability of the silica or silica gel material decrease during the heat treatment or burning treatment, and that this property decrease can be inhibited by adding a specific organic compound to the silica or silica gel prior to the heat treatment.

The present inventors have thus found that an adsorbent which combines the high ability to reversibly adsorb VOCs and high hydrophobicity can be realized from silica or a silica gel as an inexpensive raw adsorbent material.

In order to accomplish the above objects, another adsorbent according to the present invention comprises a porous molded silica gel having been obtained by adding at least one organic compound selected from the group consisting of carboxylic acids and derivatives thereof, aldehydes and derivatives thereof, and thermally

decomposable high-molecular organic compounds to a raw silica gel in an amount of from 1 to 30% by weight based on the adsorbent and then heat-treating the mixture at a temperature of from 400 to 750°C and having a specific surface area of from 450 to 700 m^2/g and an average pore diameter of from 1.7 to 5.5 nm, and selectively adsorbs volatile organic compounds having 1 to 12 carbon atoms.

Another process for adsorbent production according to the present invention is a process for preparing an adsorbent comprising silica as the main component and selectively adsorbing volatile organic compounds having 1 to 12 carbon atoms, comprising:

an addition step in which at least one organic compound selected from the group consisting of carboxylic acids and derivatives thereof, aldehydes and derivatives thereof, and thermally decomposable high-molecular organic compounds is added to a raw silica gel in an amount of from 1 to 30% by weight based on the adsorbent, and

a heat treatment step in which the silica gel to which the compound has been added is kept at a temperature of from 400 to 750°C for a predetermined period of time.

Preferably, the above process comprises, prior to the heat treatment step, a molding step in which the

silica gel after the addition step is molded to obtain a molded silica gel. Furthermore, in the heat treatment step, the silica gel to which the compound has been added is preferably heated to the predetermined temperature at an average heating rate of from 0.5 to 20 °C/min.

The present inventors further made intensive studies in order to eliminate the problems described above. As a result, they have succeeded in inventing an adsorbent having specific values of specific surface area and average pore diameter and having a high VOC-adsorbing ability and high hydrophobicity by depositing a specific amount of a specific metal on a silica gel used as an inexpensive, noncombustible, raw adsorbent material and heat-treating the silica gel.

Namely, in order to accomplish the above objects, still another adsorbent according to the present invention comprises a molded silica gel having been obtained by incorporating at least one metal selected from aluminum, zirconium, and titanium into a silica gel in such an amount that the ratio of the number of metal atoms in the silica gel to the number of silicon and metal atoms therein is from 200:1 to 4000:1 and then heat-treating the resultant mixture at a temperature in the range of from 300 to 700°C and having a specific

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surface area of from 400 to 600 m^2/g and an average pore diameter of from 1.0 to 4.0 nm, and selectively adsorbs volatile organic compounds having 1 to 12 carbon atoms.

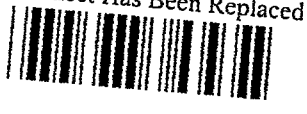
A process for preparing an adsorbent according to the present invention from a molded silica gel or powdery silica gel as a raw material is a process for preparing an adsorbent selectively adsorbing volatile organic compounds having 1 to 12 carbon atoms, comprising:

a deposition step in which either at least one metal selected from aluminum, zirconium, and titanium or a compound of the metal is deposited on a molded or powdery silica gel having a specific surface area of 550 m^2/g or more and an average pore diameter of from 1.0 to 4.0 nm in such an amount that the ratio of the number of metal atoms in the silica gel to the number of silicon and metal atoms therein is in the range of from 200:1 to 4000:1 and

a heat treatment step in which the molded silica gel after the deposition step is heat-treated at from 300°C to 700°C.

For practical use, the above process further comprises, prior to the heat treatment step, a step in which the powdery silica gel after the deposition step is molded to form a molded silica gel.

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When a metal is incorporated into a molded silica gel by the impregnation method, the above process further comprises, prior to the deposition step, a pretreatment step in which the molded silica gel is preliminarily heat-treated at a temperature of from 500 to 700°C so as to prevent the silica gel from cracking.

The present inventors still further made intensive studies. As a result, they have found that in an adsorptive method for recovering a gaseous hydrocarbon contained in a waste gas, when a desorbed gas is cooled to ordinary temperature and the resultant uncondensed gas containing the gaseous hydrocarbon is returned to the inlet of the adsorber to repeatedly recycle the same, then the gaseous hydrocarbon in the desorbed gas is gradually concentrated and part thereof eventually condenses upon cooling to ordinary temperature. The present invention has thus been completed.

Namely, the present invention provides a method for adsorptively recovering a hydrocarbon vapor contained in a waste gas or the like using cooling condensation, comprising:

(A) cooling a desorbed gas to ordinary temperature, returning the resultant uncondensed gas containing a gaseous hydrocarbon to the inlet of an adsorber, mixing

the uncondensed gas with a gas to be treated to heighten the concentration of the gaseous hydrocarbon in the gas to be treated, and sending the resultant mixture to the adsorber to conduct an adsorption step,

(B) subsequently conducting desorption to yield a desorbed gas containing the gaseous hydrocarbon in a higher concentration than a desorbed gas to be obtained when the gas to be treated is treated alone,

repeating (A) and (B) above to thereby condense a part of the hydrocarbon contained in the desorbed gas by cooling to ordinary temperature, and recovering the condensed hydrocarbon.

The adsorbents for adsorbing the gases of volatile organic compounds (hereinafter referred to simply as "adsorbents") of the present invention can be used for the adsorption of VOCs generating from medium to light fractions such as gasolines, naphthas, kerosenes, gas oils, and the like. Since the adsorbents have high hydrophobicity and a high VOC-adsorbing ability, they are suitable for use as adsorbents in the adsorption of VOCs emitted from gas stations, oil tank stations, and the like, especially by a PSA process.

The term "VOCs" in the present invention means the gases of volatile organic compounds having 1 to 12 carbon atoms. The term "VOC-adsorbing ability" means

the ability to adsorb VOCs. The term "volatile organic compounds" means hydrocarbons, halogenated hydrocarbons, and oxygen-containing organic compounds. The oxygen-containing organic compounds are organic compounds containing at least one of -O- and =O in the chemical formula, such as alcohols, ethers, esters, carboxylic acids, ketones, aldehydes, and the like.

The values of specific surface area, pore volume, and average pore diameter as measures of the porosity characteristics of the adsorbents of the present invention were determined by the BET method.

The waste gas containing one or more gaseous hydrocarbons, in the present invention, is not particularly limited. Waste gases ranging from one containing one or more gaseous hydrocarbons in a low concentration of from several tens to several thousands ppm to one having a gaseous-hydrocarbon concentration as high as about 30% can be used. Examples thereof include waste gases generating in facilities where volatile hydrocarbons are landed or loaded, such as oil tank stations and the like, and facilities where solvents are handled for coating, printing, and the like. Specific examples thereof include waste gases containing gasoline vapor, benzene, toluene, MEK, ethyl acetate, dichloromethane, methanol, and the like.

Raw Material for Adsorbents

The raw material for the adsorbents of the present invention is silica or a silica gel each having a specific surface area of 600 m^2/g or more, preferably 650 m^2/g or more, a pore volume in the range of from 0.05 to 0.5 cm^3/g, preferably from 0.1 to 0.3 cm^3/g, and an average pore diameter in the range of from 0.4 to 3.0 nm, as determined by the BET method using nitrogen molecules as a probe.

The term "silica" means one containing no water, while the term #silica gel" means one containing water. The adsorbents and the raw material therefor each may contain inorganic ingredients other than silica or a silica gel so long as the objects of the present invention are accomplished.

The substantial upper limit of the specific surface areas of the silica gel materials available on an industrial scale is about 800 m^2/g at present. However, the larger the specific surface area, the higher the adsorbing ability.

Average Pore Diameter of Raw Material

That an adsorbent has a large specific surface area means that the adsorbent has, per unit weight or

unit bulk volume, a large area available for the adsorption of VOC molecules. Namely, such an adsorbent has an accordingly increased adsorption capacity. Consequently, when high-concentration VOCs are to be adsorbed, an adsorbent having a large specific area may be used. On the other hand, when low-concentration VOCs which have volatilized and diffused into air are to be adsorbed as in the present invention, it is important that optimal pore diameters which facilitate VOC adsorption should be imparted to an adsorbent besides a large specific surface area. This is because VOC molecules are thought to be adsorbed by capillary condensation in relatively small pores. It is therefore important for an adsorbent to not only have a large surface area but have such porosity that the pores thereof have a small average pore diameter so as to attain a high probability of contact with VOC molecules and enable a condensation step to proceed efficiently.

From the above standpoint, the average pore diameter of the raw silica gel or silica is preferably from 0.4 to 3.0 nm, more preferably from 0.6 to 1.5 nm. In the BET method, nitrogen molecules are generally used frequently. In this case, the lower limit of pore size in determining pore volume or pore distribution is that of a gap or pore which nitrogen molecules can enter.

Pore Volume of Raw Material

In order for the raw silica or silica gel to have an optimal average pore diameter, the pore volume thereof is preferably from 0.05 to 0.5 cm^3/g, more preferably from 0.1 to 0.3 cm^3/g, which is determined from correlation among the specific surface area, pore volume, and average pore diameter thereof.

If the pore volume thereof exceeds that, the resultant adsorbent has too large a pore diameter to enable smooth adsorption of VOC molecules. Conversely, if it is smaller than 0.05 cm^3/g, the resultant adsorbent has too small a pore diameter to enable VOC molecules to readily enter the pores.

Shape of Raw Material Pellets

The raw material for the adsorbents of the present invention may have any of various shapes, such as spherical, cylindrical, tablet shapes, and the like. All such shapes can be advantageously used. Although a silica powder or a silica gel powder can be used, it is preferred to mold the powder into any of various shapes before use. Preferably used molding techniques include general molding methods, such as compression molding,

extrusion molding, and the like. A binder may be suitably added in order to facilitate molding.

The size of the moldings is determined by factors including the size of a layer of the packed adsorbent and the allowable differential pressure. However, the diameter and length thereof each is preferably from 2 mm to 10 mm, more preferably from 3 mm to 8 mm. If the diameter or length thereof is less than that, too high a differential pressure results. If it exceeds that, the result is too large spaces among the moldings.

The raw silica gel or raw silica having the properties shown above is subjected to a given hydrophobizing treatment, whereby an adsorbent of the present invention can be obtained. In the hydrophobizing treatment, the raw material is heated to a predetermined heat treatment temperature in the specified range at a heating rate in the specified range, and is held at the predetermined heat treatment temperature for a predetermined period of time. The predetermined heat treatment temperature need not be constant throughout the predetermined period of time, and may fluctuate within the specified temperature range.

The heating rate may be from 1 to 20 °C/min, and preferably from 5 to 15 °C/min. If the heating rate is more than that, the raw material particles each has an

increased temperature difference between the surface and an inner part thereof, so that there is a high possibility that the raw material particles might break. In addition, since such particles thus deform, the resultant adsorbent is apt to break upon water adsorption. Furthermore, heating rates more than 20 °C/min are undesirable in that there is a fear that the temperature of the raw material may exceed the predetermined temperature range (overshooting) when the operation shifts from heating to temperature keeping. Conversely, even if too low a heating rate is used, there is theoretically no problem. However, the substantial lower limit is 1 °C/min because of a reason of economy, i.e., such low heating rates result in low productivity.

Heat Treatment Temperature and Keeping Period

After the raw material particles have been heated to the specified heat treatment temperature, the temperature is maintained in that temperature range for 2 to 5 hours to burn the raw material particles. During this period, sufficient care should be taken to control the temperature. The range of heat treatment (burning) temperature is preferably from 550°C to 700°C, more

preferably from 600°C to 700°C, and most preferably from 620°C to 700°C.

The burning period is not limited as compared with the temperature conditions. However, the burning period is preferably from 2 to 5 hours, more preferably from 3 to 5 hours.

It is thought that the hydrophobizing of silica or a silica gel proceeds when many silanol groups (Si-OH) present on the surface of the silica or silica gel are caused to undergo either or both of the decomposition/elimination reaction and the condensation reaction shown by the following schemes (1) and (2). For enabling these reactions to proceed sufficiently, it is necessary to keep the silica or silica gel at a predetermined temperature within the above temperature range for a predetermined period of time.

$(SiOH)_n \rightarrow SiO_2$ decomposition/elimination (1)

$(SiOH)_n \rightarrow (Si\text{-}O\text{-}Si)_{n/2}$ condensation (2)

If the heat treatment temperature exceeds the upper limit of the specified temperature range, sintering of the silica or silica gel proceeds considerably, resulting in a decrease in specific surface area exceeding 40%. As a result, the desired porosity characteristics cannot be obtained. Conversely, if it is lower than the lower limit of the temperature

range, the hydrophobizing treatment is insufficient and there is hence a high possibility that the resultant adsorbent might break during pressure swing cycles in a PSA process.

Compared to the temperature range, the range of time period for keeping is less severe. However, if it is less than 2 hours, there is a fear that the chemical reactions shown by schemes (1) and (2) may proceed insufficiently. Conversely, if it exceeds 5 hours, productivity is impaired.

The raw material is heated at the predetermined heating rate so as to prevent cracking caused by thermal expansion, or the like, and surface OH groups are removed, as shown by schemes (1) and (2), at a temperature of from 550°C to 700°C, whereby hydrophobicity is improved.

If an improvement in hydrophobicity is the only purpose, the heating and burning treatment are sufficient. However, for use in recovering low-concentration VOCs present in the air, an adsorbent should retain a large surface area and excellent hydrophobicity. Consequently, properties of the raw adsorbent material (silica or a silica gel) are important as stated hereinabove.

Decrease in Specific Surface Area

In a PSA process, adsorption is not conducted until a stationary state is reached as in the case of determining an adsorption isotherm, but is conducted while swinging the pressure for every adsorption step conducted for a given time period. It is therefore necessary to quickly adsorb VOC molecules having a low partial pressure, and adsorption rate is one of the important factors. Hence, in order to effectively adsorb VOC molecules, it is important for the adsorbent to have specific values of specific surface area, average pore diameter, and hydrophobicity. As a result, a heightened adsorption rate is obtained.

For realizing a high adsorption rate, smaller decreases in specific surface area are preferred. If the decrease in specific surface area exceeds 40%, not only the pore diameter changes due to sintering, resulting in a reduced VOC-adsorbing ability, but also the volume change arouses troubles such as cracking, deformation, *etc.* By conducting the hydrophobizing heat treatment under the conditions shown above, the decrease in specific surface area as shown by equation (3) is regulated to 40% or less and the average pore diameter after the treatment is close to that of the raw silica gel. Thus, an adsorbent combining excellent

hydrophobicity and an excellent VOC-adsorbing ability and having a high adsorption rate is realized.

Decrease in specific surface area (%) =

(specific surface area of raw silica)

/(specific surface area after heat treatment)

× 100 (3)

Water Vapor Adsorption

When an adsorbent adsorbs water vapor in an amount of 10 ml/g or more in adsorption equilibrium at 20°C and a water vapor pressure of 2 mmHg, it frequently cracks. Although an adsorbent after the hydrophobizing treatment in a process of the present invention can have a water vapor adsorption reduced to 10 ml/g or less, it is difficult to reduce the water vapor adsorption to 3 ml-water-vapor/g-adsorbent or smaller.

Modes of Using Adsorbents

When an adsorbent is actually used in a PSA system, the amount of the adsorbent to be packed, the packing height, and the like are suitably determined according to operation conditions such as the volume and number of adsorption columns, the VOC concentration in an inlet gas, the percentage of VOC capture, operation temperature, and the like.

Even when the adsorbents of the invention are used in combination with or as a mixture with a known adsorbent, such as a high-silica zeolite, alumina, or the like, this does not pose a problem. However, since the market prices of such other adsorbents are higher than that of the adsorbents of the invention, the cost advantage of the adsorbents of the present invention is lost if the amount of a known adsorbent mixed or combined therewith is large.

No activation treatment is necessary for the adsorbents of the present invention before use. When the adsorbents have been stored for long in an atmosphere having an exceedingly high humidity, it is sufficient to suitably conducting vacuum drying treatment at a temperature of from ordinary temperature to 350°C. Although the time period for the vacuum drying varies depending on PSA apparatuses, the actual range thereof is from 1 to 24 hours.

VOC Selectivity of Adsorbent

The term "VOC selectivity of an adsorbent" as used in the present invention means the proportion of the amount of a volatile organic compound adsorbed on the adsorbent to that of water vapor and the volatile

organic compound adsorbed thereon. The selectivity is a value defined by the following equation.

$$\text{VOC selectivity} = \{(A)/(A + B)\} \times 100$$

In the above equation, A is the equilibrium adsorption (ml/g (stp)) of the volatile organic compound on the adsorbent at a temperature of 20°C and a pressure which is one-tenth the saturation vapor pressure of the volatile organic compound at a temperature of 20°C.

B is the equilibrium adsorption (ml/g (stp)) of water vapor on the adsorbent at a pressure of 2 mmHg and a temperature of 20°C.

In the present invention, the equilibrium adsorption of a volatile organic compound (VOC) on an adsorbent is determined not at the saturation vapor pressure of the VOC but at a pressure which is one-tenth the saturation vapor pressure of the VOC. This is because the VOC is mostly adsorbed onto the adsorbent before the pressure reaches one-tenth the saturation vapor pressure. Namely, the reason for the above is that virtually, (adsorbed amount at the saturation vapor pressure) ≒ (adsorbed amount at a pressure one-tenth the saturation vapor pressure).

In addition, in practicing PSA operation by the pressure swing method, an adsorption step is usually conducted until the pressure reaches a value not larger

than one-tenth the saturation vapor pressure of a VOC (a pressure lower than the one-tenth is usable), without pressurizing the gas to the saturation vapor pressure of the VOC, before the adsorption step is shifted to a desorption step.

As apparent from the above, VOC selectivity is defined as a factor which indicates the efficiency of VOC adsorption in PSA operation.

Physically, the higher the VOC selectivity of an adsorbent, the more the adsorbent adsorbs the volatile organic compound in the presence of water vapor. Such an adsorbent can be regarded as an excellent adsorbent for the PSA of VOCs. Consequently, the adsorbents have a VOC selectivity of 80% or more, preferably 85% or more. The adsorbents having a VOC selectivity of 80% or more can be used in a smaller amount than adsorbents having a low VOC selectivity, and are markedly advantageous in the profitability and operation efficiency of a PSA process.

Besides the VOC selectivity described above, VOC adsorption amount also is an important factor for an adsorbent.

For example, if an adsorbent has a high VOC selectivity but a small VOC adsorption, this poses problems, for example, that the adsorbent amount

necessary for separating and recovering a given amount of the VOC is too large. Consequently, an adsorbent should have a high VOC selectivity and show a VOC adsorption amount not below a given level.

VOC adsorption amount is evaluated in terms of the equilibrium adsorption (ml/g (stp)) of the volatile organic compound on the adsorbent at a temperature of 20°C and a pressure which is one-tenth the saturation vapor pressure of the volatile organic compound at a temperature of 20°C. This VOC adsorption is measured by the same method as that shown as the method for determining VOC selectivity.

A preferred adsorbent is one in which the equilibrium adsorption of a volatile organic compound on the adsorbent at a temperature of 20°C and a pressure which is one-tenth the saturation vapor pressure of the volatile organic compound at a temperature of 20°C is 30 ml/g (stp) or more. A more preferred adsorbent has an equilibrium adsorption of 35 ml/g (stp) or more.

If an adsorbent having a VOC adsorption smaller than that is used, the adsorbent amount required for the apparatus to obtain the same effect should be increased, so that larger adsorption columns are necessary and the sizes of instruments and devices attached to the apparatus should also be increased. As a result, the

whole apparatus comes to have an increased size and there is a high possibility that the operation cost might increase due to an increased power consumption, *etc.* Conversely, there is no particular upper limit. However, the current upper limit is thought to be around 150 ml/g (stp).

Raw Silica Gel

The silica gel for use as a raw material for the adsorbents of the present invention may be any silica gel so long as it is a dry gel comprising colloid particles of silica (SiO_2), such as an aerogel composed of innumerable particles (primary particles) of amorphous silicon dioxide (= silica [SiO_2]) bonded to each other to form a porous structure, a silica gel comprising the aerogel matrix partly containing water, a silica gel comprising the aerogel matrix having crystal water, a gel-like aggregate composed of solid colloid particles formed by the dehydrating condensation of orthosilicic acid (H_4SiO_4, *etc.*), and the like.

A commercial product of silica gel or silica as it is can be used as the silica gel as a raw adsorbent material in the present invention. Besides these, the raw adsorbent material may be a silica gel obtained by mixing sodium silicate (water glass) with a mineral acid

(sulfuric acid, hydrochloric acid, *etc.*) to prepare a silica hydrosol and converting the same into a gel, or may be a silica gel obtained by subjecting an alkoxide, such as ethyl silicate ($Si(OC_2H_5)_4$), to hydrolysis and polycondensation to form a gel.

The raw silica gel is preferably one having a specific surface area and an average pore diameter, both determined by the BET method using nitrogen molecules as a probe, of 500 m^2/g or more and 5 nm or less, respectively. It is more preferably one having a specific surface area of 680 m^2/g or more and an average pore diameter of 2 nm or less, and is even more preferably one having a specific surface area of 760 m^2/g or more and an average pore diameter of 2 nm or less.

There is no particular upper limit on specific surface area. It is however thought that the currently actually available upper limits are from 800 to 1000 m^2/g. Conversely, when a silica gel having a specific surface area smaller than 500 m^2/g is hydrophobized, there is a fear that the reversible adsorption (δq) of VOC molecules may be insufficient.

In the case of a molded silica gel, there is no limitations on shape, and any of spherical, cylindrical, hollow, and tablet shapes and other various shapes can

be advantageously used. In the case of a powder, it preferably has such a particle diameter that the powder particles pass through a 50- to 200-mesh sieve, and more preferably has such a particle diameter that the particles pass through a 100- to 200-mesh sieve, so as not to arouse a trouble in the molding step which will be described later. A binder or the like may be added for molding.

Second Ingredients

At least one organic compound selected from the group consisting of carboxylic acids and derivatives thereof, aldehydes and derivatives thereof, and thermally decomposable organic high-molecular compounds may be added to a silica gel. Hereinafter, such ingredients to be added to a silica gel are referred to as "second ingredients".

Preferred carboxylic acids which can be used include aliphatic monocarboxylic acids, such as caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, and the like; aromatic monocarboxylic acids, such as phenylacetic acid, toluic acid, benzoic acid, and the like; alicyclic monocarboxylic acids, such as cyclohexanecarboxylic acid, cyclopentanecarboxylic acid, and the like; dicarboxylic

acids, such as phthalic acid, isophthalic acid, terephthalic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, and the like; and oxy acids having a hydroxyl group, such as tartronic acid, malic acid, tartaric acid, mandelic acid, tropic acid, and the like.

These carboxylic acids may be subjected to isomerization for, e.g., branching an alkyl group or to conversion into derivatives through, e.g., alkylation or phenylation. Such conversions may be conducted, without particular limitations, according to the necessity of modifying properties of the carboxylic acids.

Preferred aldehydes include acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, caproaldehyde, heptaldehyde, tolualdehyde, benzaldehyde, glyoxal, and the like.

In the same manner as carboxylic acids, such aldehydes may be suitably subjected, without particular limitations, to conversion into derivatives, isomerization, or the like, if the aldehydes are required to have modified properties.

The term "thermally decomposable high-molecular organic compounds" means high-molecular organic compounds which decompose in the temperature of from 400 to 750°C. Preferably used are, for example, poly(vinyl

alcohol) (PVA), poly(vinyl acetate) (PVAc), partially saponified poly(vinyl acetate) (p-PVAc), polyvinylpyrrolidone (PVP), melamine-formaldehyde resins, polyamide-formaldehyde resins, cyclodextrin (CD), cellulose acetate, methyl cellulose, carboxymethyl cellulose (CMC), and the like.

Such a thermally decomposable high-molecular organic compound may have a molecular weight (degree of polymerization) suitably selected according to availability, cost, properties, and the like.

Method of Adding Second Ingredients

Preferred methods usable for adding the seconds ingredients to a silica gel include the dry kneading, wet kneading, and impregnation methods.

When the dry kneading method is used, blending may be accomplished by sufficiently kneading a silica gel powder together with a powder of a second ingredient by means of an automatic mortar or the like.

When the wet kneading method is used, a solvent or a dispersion medium is further added to a silica gel powder besides a second ingredient, and the resultant mixture is kneaded and dried prior art to a molding step. When the second ingredient is liquid, the addition of a solvent or dispersion medium may be omitted.

The addition of a second ingredient by the impregnation method is applicable to both a molded silica gel and a silica gel powder. An explanation will be given below on an example in which water is used as a solvent for a second ingredient. When solvents other than water are used, the same method is usable.

1) Prior to the addition of a second ingredient, the saturation water absorption of a silica gel is determined in the following manner.

a) First, the silica gel is dried.

When the silica gel is a silica gel powder, the drying thereof may be accomplished by heating it at 80 to 200°C for 1 to 3 hours. A molded silica gel is dried in the following manner. The molded silica gel is immersed in a solvent to be used in the impregnation step which will be described later. When the silica gel does not crack during the impregnation period, the same drying treatment as that used for the silica gel powder is sufficient. On the other hand, when the molded silica gel cracks during the impregnation period, preheating is conducted for cracking prevention. The heating temperature and the heating period cannot be fixed unconditionally, because they vary depending on the properties of the silica gel and the kind of the

solvent used. However, the preheating is usually conducted at 300 to 400°C for 30 to 60 minutes. When the molded silica gel is less apt to crack or where a solvent less apt to cause cracking is selected, the preheating can be omitted.

b) Subsequently, the silica gel is precisely weighed.

c) The silica gel is caused to absorb water to determine the saturation water absorption.

The silica gel after drying or preheating is cooled to room temperature. Water is then dropped thereonto from a buret to cause the silica gel to sufficiently absorb water, and the saturation water absorption per silica gel weight is measured. The saturation water absorption is determined by measuring with a balance the weight of the silica gel which has been caused to sufficiently absorb water by dropping water thereonto from a pipet, dropping pipet, or the like, and subtracting the weight of the silica gel *per se* therefrom.

2) The silica gel is impregnated with a second ingredient.

Prior to impregnation with a second ingredient, the silica gel is sufficiently dried in the same manner as that used for determining the saturation water

absorption. Namely, when a silica gel powder is used, drying treatment is conducted for a given time period. When a molded silica gel is used, drying treatment is conducted optionally together with heat treatment for a given time period.

An aqueous solution of the second ingredient is prepared in the same amount as the saturation water absorption of the silica gel to be impregnated therewith. The silica gel is immersed in this aqueous solution for 0.5 hours to 1 hour. Thereafter, the excess water is removed and the silica gel is then dried.

The drying conditions vary depending on the amount of the adsorbent to be produced and the kind of the solvent. However, a practical method is to dry the silica gel at a temperature lower than the decomposition temperature of the second ingredient and complete the drying in about from 1 to 24 hours.

Besides water, a solvent in which the second ingredient to be used in the impregnation method dissolves readily can be selected as the solvent for the second ingredient. For example, a solvent in which the second ingredient has a sufficient solubility and which is easily removable may be suitably selected from alcohols, ketones, saturated hydrocarbons, alicyclic

hydrocarbons, aromatic hydrocarbons, unsaturated hydrocarbons, and the like.

As stated hereinabove, when a molded silica gel is used, it is preferred to select a solvent which causes no or little cracking.

The amount of the second ingredient is preferably from 1 to 30% by weight, more preferably from 5 to 25% by weight, and most preferably from 5 to 20% by weight, based on the adsorbent.

If the amount thereof is smaller than 1% by weight, both the hydrophobizing effect and the effect of maintaining property values of the raw silica gel are poor. Conversely, if it exceeds 30% by weight, there is a possibility that part of the second ingredient might remain undecomposed after heat treatment or the adsorbent might have impaired properties rather than improved ones.

When a powdery silica gel is used, it is molded after addition of the second ingredient. For molding, known methods such as compression molding, extrusion molding, and granulation can be advantageously used.

The shape thereof may be cylindrical, spherical, hollow, *etc.*, and may be suitably selected according to adsorption processes. Although the size thereof is not

particularly limited, the practical range thereof is thought to be about from 1.5 mm to 10 mm.

Heat Treatment

In a heat treatment step, the silica gel to which a second ingredient has been added is heated in air to a temperature in a predetermined range and subsequently held in this temperature range. The temperature for the heat treatment is preferably from 400 to 750°C, more preferably from 450 to 680°C, and most preferably from 500 to 680°C. Heating at temperatures below 400°C is undesirable in that the hydrophobizing effect is insufficient. Conversely, heating at temperatures exceeding 750°C is undesirable in that considerable property decreases including a large decrease in surface area occur and a reduced reversible VOC adsorption results, although the raw material is hydrophobized.

The average heating rate in heating to the heat treatment temperature range is preferably from 0.5 °C/min to 20 °C/min, more preferably from 1.5 °C/min to 15 °C/min, and most preferably from 3 °C/min to 10 °C/min. If it is less than 0.5 °C/min, the heat treatment has low productivity and is uneconomical because it requires too much time. Conversely, if heating is conducted at a rate of more than 20 °C/min, there is a fear that the

molded silica gel may crack. Furthermore, 20 °C/min comes under the group of considerably high heating rates in production on practical scales, and may be thought to be an upper limit.

During temperature rising, water (water vapor) and decomposition gases of the second ingredient generate. Hence, the heating rate may be changed in the course of temperature rising, or a temperature during the temperature rising may be maintained for a while.

When a molded silica gel in which the diameter or the length of a side is 3 mm or more is heat-treated at a temperature of 550 to 570°C, or more, there is a high possibility that the molded silica gel might crack due to a temperature difference between the outer and inner sides.

When a molded silica gel which suffers cracking is used, the cracking can be prevented almost completely by regulating the heating rate in heating from a temperature between 550 and 570°C to a higher temperature to 0.5 to 7 °C/min, preferably 0.5 to 5 °C/min, and more preferably 0.5 to 3 °C/min.

After the temperature of the molded silica gel has reached the predetermined temperature range, the silica gel is held at this temperature for a time period which is preferably from 2 to 5 hours, more preferably

from 3 to 4 hours, although this keeping period varies depending on the amount to be treated.

If the keeping period is less than 2 hours, there are fears, for example, that the adsorbent may have a reduced strength, that an additive may remain undecomposed, and that hydrophobizing is insufficient. Conversely, even if the keeping period is prolonged beyond 5 hours, not only this is technically meaningless because no further improvement in performance by the prolongation is expected, but also productivity is reduced.

The adsorbent for the PSA of VOCs obtained through the addition of a second ingredient and heat treatment by the method described above has a specific surface area of preferably from 450 to 700 m^2/g, more preferably from 500 to 700 m^2/g, and most preferably from 550 to 700 m^2/g, and has an average pore diameter of preferably from 1.7 to 5.5 nm, more preferably from 2.0 to 4.5 nm. The pore volume thereof is preferably from 0.2 to 0.7 ml/g.

If the specific surface area thereof is less than 450 m^2/g, the adsorbent has a reduced reversible VOC adsorption, which poses a problem that the adsorbent should be packed in a larger amount in practical use, resulting in an increased cost. Conversely, the higher

the upper limit of the specific surface area, the more preferred. However, 700 m^2/g can be regarded as the substantial upper limit because the specific surface areas of the available raw silica gels are about 800 m^2/g.

If the average pore diameter thereof is less than 1.7 nm, it is difficult to adsorb VOC molecules having a large molecular size, i.e., having a high molecular weight. Conversely, if the average pore diameter thereof exceeds 5.5 nm, the reversible adsorption amount tends to be small partly because capillary phenomenon is less apt to occur.

If the pore volume thereof is less than 0.2 ml/g, the reversible adsorption amount tends to be too small. Conversely, if the pore volume exceeds 0.7 ml/g, it is difficult to ensure a necessary specific surface area because an increase in pore volume generally tends to result in a decrease in specific surface area. Adsorbents having such an increased pore volume have another drawback that capillary phenomenon is less apt to occur.

The mechanisms of the production of a hydrophobizing effect by the addition of a second ingredient are unclear. However, the following mechanism can be presumed. During heat treatment, the

second ingredient decomposes to generate reactive decomposition species such as methyl radicals (alkyl radicals). These active species are subjected to some reaction with hydrophilic groups such as silanol groups (SiOH) on the silica gel surface to yield methyl groups (alkyl groups), which are hydrophobic, on the surface.

It is also presumed that the functional groups of the carboxylic acid, aldehyde, or thermally decomposable high-molecular compound interact with hydrophilic groups (SiOH groups) on the silica gel surface to generate active decomposition species around the hydrophilic groups to thereby hydrophobize the surface.

In addition, it is thought that hydrophilic groups present on the silica gel surface is subjected to dehydrating condensation upon heating to form a kind of ether bonds. It is thought that these mechanisms in combination produce a hydrophobizing effect.

It is further thought that in heat treatment in a low-temperature range of about from 400 to 500°C, the second ingredient reacts with hydrophilic groups present on the silica gel surface to produce a hydrophobizing effect, and that in heating at temperatures beyond that temperature range, a combination of the hydrophobizing by the reaction of the second ingredient with

hydrophilic groups and the thermal condensation of hydrophilic groups produces a hydrophobizing effect.

In the case of heat treatment in a high-temperature range of 500°C or more, gaseous ingredients generated by the pyrolysis of the second ingredient are emitted from inner parts of the molded silica gel to facilitate the retention of porosity. As a result, sintering by heating is inhibited and the original properties inherent in the raw silica gel can be maintained relatively satisfactorily.

Since the properties of the silica can be maintained even through heat treatment in a high-temperature range in the present invention, the molded silica gel is effectively hydrophobized by the decomposition and condensation of the silanol groups present on the surface thereof and by the presence of hydrophobic alkyl groups or the like remaining on part of the surface thereof.

As described above, both a hydrophobizing effect and a property-maintaining effect are produced by adding a second ingredient to a molded silica gel or silica gel powder and then subjecting the resultant mixture to molding and heat treatment. As a result, an adsorbent for the PSA of VOCs is obtained which shows an exceedingly high performance.

Raw Silica Gel

The silica gel for use as a raw material for the adsorbent of the present invention (claim 8) may have either of a molded form and a powder form. The silica gel is not particularly limited in the material constituting the same so long as it is a dry gel comprising colloid particles of silica (SiO_2). For example, use can be made of an aerogel composed of innumerable particles (primary particles) of amorphous silicon dioxide (= silica [SiO_2]) bonded to each other to form a porous structure, a silica gel comprising the aerogel matrix partly containing water, a silica gel comprising the aerogel matrix having crystal water, and a gel-like aggregate composed of solid colloid particles formed by the dehydrating condensation of orthosilicic acid (H_4SiO_4, *etc.*).

A commercial product of silica gel or silica as it is can be used as the silica gel as a raw adsorbent material in the present invention. Besides these, the raw adsorbent material may be a silica gel obtained by mixing sodium silicate (water glass) with a mineral acid (sulfuric acid, hydrochloric acid, *etc.*) to prepare a silica hydrosol and converting the same into a gel, or may be a silica gel obtained by subjecting an alkoxide,

such as ethyl silicate ($Si(OC_2H_5)_4$, *etc.*), to hydrolysis and polycondensation to form a gel.

The raw silica gel is preferably one whose specific surface area, pore volume, and average pore diameter as determined by the BET method using nitrogen molecules as a probe are within the respective ranges shown below.

The larger the specific surface area of the raw silica gel, the larger the specific surface area and VOC adsorption of the product adsorbent. Conversely, if the raw silica gel has a small specific surface area, it is difficult to produce a product adsorbent having a practical VOC adsorption. It is therefore necessary to use a raw silica gel having a specific surface area of 550 m^2/g or more.

The upper limit of the specific surface areas of the actually available silica gels is thought to be about 1000 m^2/g. Consequently, the specific surface area of the raw silica gel is preferably from 550 m^2/g to 850 m^2/g, especially more preferably from 700 to 850 m^2/g, in view of availability, adsorbent performance, and the like.

As will be seen from Examples and Comparative Examples, the difference in average pore diameter between the raw silica gel and the product adsorbent is

extremely small, and the average pore diameter decreases little in the course of adsorbent production. Consequently, the average pore diameter of the raw silica gel can be determined in view of the average pore diameter of the product adsorbent.

The average pore diameter of the raw silica gel is preferably 4.0 nm or less. This is because the smaller the average pore diameter of a raw silica gel, the larger the specific surface area of the product adsorbent. In view of the sizes of VOC molecules, the substantial lower limit of the average pore diameter of the raw silica gel is 0.3 nm. Smaller average pore diameters are preferred in that the smaller the average pore diameter of a product adsorbent, the more the capillary condensation of VOCs is apt to occur. However, the rate of diffusion of VOCs in such fine pores is low, resulting in a reduced VOC adsorption rate. Conversely, the larger the average pore diameter, the higher the porosity and the lower the mechanical strength of the product adsorbent. In view of the mechanical strength of the product adsorbent, the rate of VOC adsorption, *etc.*, the average pore diameter of the raw silica gel is preferably from 1.0 to 4.0 nm, more preferably from 1.2 to 2.5 nm.

The raw silica gel need not be particularly limited in pore volume. This is because when the specific surface area and the average pore diameter are fixed, a rough value of pore volume is naturally determined.

Specifically, when the specific surface area and the average pore diameter are fixed to values within the ranges shown above, the preferred range of pore volume is from 0.20 to 0.70 ml/g. Furthermore, in view of the mechanical strength and VOC adsorption capacity of the adsorbent, and the like, the more preferred range thereof is from 0.30 to 0.65 ml/g and, in particular, the most preferred range thereof is from 0.30 to 0.45 ml/g.

Metal Contained

A product adsorbent of the present invention has a metal deposited thereon in the form of metal atoms or a metal compound converted from a metal salt or another metal compound which was deposited on a silica gel during production. The term "metal" in the present invention means a metal element *per se* such as aluminum [Al], zirconium [Zr], titanium [Ti], or the like, while the term "metal salt" means a metal compound such as,

e.g., aluminum nitrate nonahydrate, zirconium oxynitrate dihydrate, or titanium sulfate.

Preferred salts of aluminum, zirconium, and titanium metals are nitrates, oxynitrates, carbonates, sulfates, acetates, lactates, and the like. The nitrates of the metals are more preferred. Since these metal salts in either the anhydrous or a hydrated form can be advantageously used, more easily available substances may be used.

However, the chlorides, among the metal salts, are undesirable in that they have no cost advantage over the other metal salts and conversely have drawbacks, for example, that chlorine radicals may remain in the adsorbent and that chlorine and other substances generate during the heat treatment which will be explained next.

Field of Application of Adsorbents according to the Invention

The adsorbents of the present invention are suitable for use as adsorbents for the recovery of VOCs generating, for example, from liquid organic compounds, such as organic solvents for coating and chlorinated organic solvents for cleaning, from fuels for transportation, such as gasolines, kerosenes, gas oils,

and the like, or from liquid organic solvents used in printing. The term "VOC" as used in the present invention means a volatile organic compound gas having 1 to 12 carbon atoms, and the term "VOC-adsorbing ability" means the ability to adsorb a VOC.

The adsorbents of the present invention can be advantageously used as adsorbents in practicing known adsorption methods, such as PSA process, TSA process, PTSA process, and the like.

Details of Production Process

A process for preparing an adsorbent according to the present invention basically comprises a metal deposition step (metal salt addition step) and a heat treatment step. It preferably has a pretreatment step in which a molded silica gel or a powdery silica gel is preliminarily heat-treated at a temperature of from 500 to 700°C.

Pretreatment Step

The heat treatment prior to the metal deposition step is conducted for the purposes of, for example, temporarily removing the water contained in the raw silica gel so as to enable an aqueous metal solution to sufficiently infiltrate into the pores of the raw silica

gel in the metal salt addition step, and enhancing the strength of the raw silica gel through burning so as to prevent the raw silica gel from cracking during impregnation in the metal salt addition step.

Higher heating temperatures facilitate reactions between the metal salt and the silica gel surface to diminish the silanol groups remaining on the surface of the raw silica gel, although this effect is influenced by the properties of the raw silica gel. As a result, water adsorption is reduced and the VOC adsorption inhibitory effect of adsorbed water is lessened. Namely, the adsorbent surface can be effectively used to adsorb VOCs. On the other hand, the higher the heating temperature, the larger the decrease in surface area caused by sintering.

The range of heating temperature suitable for maintaining a moderate surface area and moderately removing surface silanol groups is preferably from 500 to 700°C, more preferably from 500 to 680°C, and especially most preferably from 550 to 650°C. Although the heating period varies with heating temperature, heating for from 1 to 24 hours is sufficient. Any heating rate may be used for heating to the heating temperature so long as the raw silica gel is prevented from suffering sintering caused by an abrupt temperature

rise. Preferably, the heating rate is from 0.1 to 3.0 °C/min. The heat treatment need not be necessarily conducted in an inert gas atmosphere, and may be conducted in air.

The pretreatment of a silica gel is conducted according to need for the purposes of imparting water resistance, mechanical strength, and the like. This treatment is not always necessary to a powdery silica gel to which a metal salt is to be added through kneading.

Metal Salt Addition Step

Methods for adding a metal are not limited so long as the metal can be deposited on a silica gel. However, the impregnation method is practical for molded silica gels, while kneading methods such as dry kneading or wet kneading and the impregnation method are applicable to powdery silica gels.

When a metal is added by dry kneading, a silica gel and a given amount of a metal salt are sufficiently kneaded with an automatic mortar or the like.

When a metal is added by wet kneading, a given amount of a metal salt and a dispersion medium, such as water, a liquid organic compound, or the like, are added to a silica gel to prepare a slurry, which is

sufficiently kneaded with an automatic mortar or the like and then dried. It is preferred that prior to the addition, the silica gel and the metal salt each be sufficiently ground down with an automatic mortar or the like.

A method for adding a metal by the impregnation method will be explained below. In the case of the impregnation method, the saturation water absorption of a silica gel is determined first.

Measurement of Saturation Water Absorption

An example of methods for determining saturation water absorption is shown below. A silica gel from which water has been removed by the pretreatment or sufficient drying is caused to absorb pure water until saturation to determine the water absorption per dry weight of the silica gel. The saturation with water is desirably conducted while taking sufficient time. For example, the silica gel is allowed to stand for 30 minutes to 1 hour after completion of an operation for water absorption, and the resultant state in which further water absorption is impossible is regarded as an end point. The amount of water in this state is taken as the saturation water absorption.

Since saturation water absorption varies considerably depending on properties of silica gels, it is desirable to obtain an average value after conducting the water absorption test several times. The saturation water absorption may be determined by measuring the volume with a measuring device, such as a buret or the like, or by measuring the weight with a balance or the like. When a solvent other than water, for example, an organic solvent such as an alcohol, e.g., methanol or ethanol, a ketone, or the like, is used, the solvent adsorption, which has the same meaning as saturation water absorption, can be determined through the same operation as for water.

Preparation of Impregnating Solution (Metal Salt Solution) and Impregnation Step

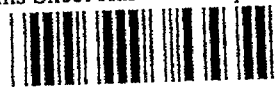
A given amount of a silica gel is weighed out. Water is weighed out in the same amount as the saturation water absorption for that amount of the silica gel. A given amount of a metal salt to be added is dissolved in the water to prepare an impregnating solution. The given amount of the weighed silica gel is immersed in the aqueous metal salt solution prepared, and is allowed to stand for a sufficient time period to impregnate the same. The impregnation period is not

shorter than the water absorption period required for determining the saturation water absorption.

After completion of the impregnation, the excess solution is removed and the impregnated silica gel is dried. The drying is conducted at a temperature lower than the decomposition temperature of the metal salt and at ordinary or a reduced pressure. The drying is usually conducted at around 100°C and ordinary pressure in the air atmosphere. The drying period is about from 1 to 24 hours although it varies depending on the amount of the silica gel.

In order to hydrophobize the adsorbent in the later heat treatment step, the metal salt should be added in such an amount as to sufficiently react with the surface OH groups of the adsorbent, although the addition amount thereof is influenced by the reactivity characteristic of the metal, the heating temperature, and the like. However, if the metal salt amount is too large, the excess metal salt accumulates on the silica to impair the adsorbent performance. Consequently, the metal is added in such an amount that the ratio of the number of metal atoms in the silica gel to the number of silicon and metal atoms therein is from 200:1 to 4000:1, preferably from 400:1 to 3200:1. The metal is at least one of aluminum, zirconium, and titanium.

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In this description, the term "atom number ratio" is used to indicate the ratio of the number of metal atoms (aluminum [Al], zirconium [Zr], titanium [Ti]) in a silica gel to the number of metal atoms and silicon [Si] atoms therein. On the assumption that the raw metal salt has been wholly decomposed and is present as the metal on the surface of the silica gel in an adsorbent state, the atom number ratio is calculated from the feed amounts of the raw silica gel and the raw metal salt using the following equation.

Namely,

Atom number ratio = Si : M

= Si mol : M mol

M = metal atoms in raw metal salt (number)

Si = metal atoms in raw metal salt (number)

+ silicon atoms in raw silica gel (number)

M mol = moles of metal in raw metal salt (number)

Si mol = moles of metal in raw metal salt (number)

+ moles of silicon in raw silica gel (number),

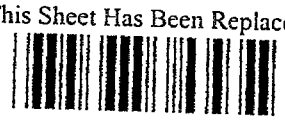
provided that 1 mol = 6.022×10^{23} atoms.

For example, when 100 g of a silica gel and 0.62 g of aluminum nitrate nonahydrate [$Al(NO_3)_3 \cdot 9H_2O$] are used as raw materials, then

the number of moles of silicon in the raw silica gel

= 100 ÷ 60.08 (molecular weight of silica [SiO_2]

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in silica gel)

= 1.664 (mol), and

the number of moles of the metal in the raw metal salt

= 0.62 ÷ 375.1 (molecular weight of aluminum nitrate nonahydrate)

= 1.653×10^{-3} (mol).

Consequently,

atom number ratio = 1.653×10^{-3}: (1.653×10^{-3} + 1.664)

= 1:1008

is 1:1000.

Molding Step

The silica gel, especially powdery silica gel, to which a metal salt has been added is molded according to need. The purposes of this molding are, for example, to impart mechanical strength to the adsorbent and to reduce the pressure loss of the adsorbent packed into adsorption columns.

Known molding methods, such as pelletizing, extruding, and the like, to mold the silica gel into an appropriate size. For example, in preparing an adsorbent for ordinary PSA, the molded silica gel has a length and a diameter of about from 2 mm to 10 mm. A

binder may be added for molding so long as the binder does not impair the performance of the adsorbent.

Heat Treatment Step

The silica gel to which a metal salt has been added is heat-treated. This step is intended to cause the metal salt and the silica gel to interact with each other to thereby hydrophobize the silica gel.

The heating temperature may be any temperature so long as the metal salt can decompose and sufficiently interact with silanol groups present on the surface of the silica gel, and is preferably from 300 to 700°C. The range of temperature for the heat treatment is influenced by the decomposability of the metal salt, hence the kind of the metal salt, addition method, properties of the raw silica gel, *etc.* However, at temperatures of 300°C or less, the metal salt does not decompose completely and the metal salt added remains partly or wholly in the original state, so that the hydrophobicity is impaired, rather than improved. Consequently, the temperature for the heat treatment is at least 300°C.

For example, when the kneading method was used for adding a metal salt, the heat treatment is conducted at a relatively high temperature because the area in

°C/min, and most preferably from 0.1 to 3.0 °C/min. A heat treatment period of about from 3 to 24 hours is sufficient.

The heat treatment can be preferably conducted in air, in an inert gas atmosphere, such as nitrogen, helium, or the like, or in a reducing gas atmosphere, e.g., hydrogen or carbon monoxide, at ordinary or a reduced pressure.

As stated above, the heat treatment is conducted for the purpose of causing the metal salt and the silica gel to interact with each other to thereby hydrophobize the silica gel. The metal salt decomposes upon the heat treatment and interacts with silanol groups present on the surface of the silica gel to thereby diminish the surface silanol groups. As a result, the adsorbent comes to have hydrophobicity.

It is thought that on the adsorbent which has undergone the heat treatment, most of the metal is scatteringly present on the silica gel surface in the form of elemental metal or metal oxide, although the state of the metal varies depending on the heat treatment conditions, such as temperature, atmosphere, and the like.

For example, when the heat treatment was conducted in the presence of oxygen, the proportion of

which the raw silica gel is in contact with the metal salt is smaller than in the impregnation method. Consequently, the heat treatment temperature is, for example, preferably from 500 to 700°C, more preferably from 500 to 680°C, and especially most preferably from 550 to 650°C.

On the other hand, when the impregnation method was used for adding a metal salt, the area in which the raw silica gel is in contact with the metal salt is larger than in the kneading method. Even at a relatively low heat treatment temperature, the metal salt and the silica gel surface hence interact with each other sufficiently. Consequently, the heat treatment temperature is, for example, preferably from 300 to 550°C, more preferably from 300 to 500°C, and most preferably from 300 to 400°C. If heating is conducted at a high temperature exceeding 550°C, the adsorbent has a reduced surface area and a reduced VOC-adsorbing ability and suffers troubles, such as cracking, deformation, and the like, caused by a volume change.

Any heating rate may be used for heating to the heat treatment temperature so long as the raw silica gel is prevented from suffering sintering caused by an abrupt temperature rise. The heating rate is preferably from 0.1 to 20 °C/min, more preferably from 0.1 to 10

the metal oxide is relatively large. Conversely, when the heat treatment was conducted in a reducing gas atmosphere, the proportion of the elemental metal is relatively large.

When a carbon-containing compound, such as carbonic acid salt, lactic acid salt, or the like, is used as a metal salt, the carbon contained in the compound is mostly removed as carbon dioxide when heat treatment is conducted in the presence of oxygen. On the other hand, when a carbon-containing compound is used and heat treatment is conducted in the absence of oxygen, the carbon is relatively less removed. In this case, a part of the residual carbon may form ether bonds on the adsorbent after the heat treatment, and silanol groups present on the silica gel surface are substituted by these ether bonds. As a result, the surface silanol groups are diminished and the adsorbent comes to have hydrophobicity.

It is extremely difficult to prove the above-described mechanism of metal salt decomposition based on instrumental analyses because the metal salt is added in a minute amount. However, it is after all thought that the metal salt decomposes upon heat treatment and interacts with silanol groups present on the silica gel

surface to diminish the surface silanol groups to thereby impart hydrophobicity to the adsorbent.

In the present invention, either a fluidized bed process or a fixed bed process may be used as an adsorption method. However, a fixed bed process is preferred. Furthermore, for adsorption and regeneration, any of TSA, PSA, and PTSA processes can be used, but a PSA or PTSA process is preferred. The adsorption methods are not particularly limited in the type of column constitution. Examples of the column constitutions thereof include a two-column type composed of one column for adsorption and one for desorption and a three-column type composed of one column for adsorption and two for desorption. Among these, the three-column type is preferred because it is effective in reducing the amount of a purge gas used in the desorption step which will be described later. An example of such adsorption methods is a process in which adsorbers for alternately conducting adsorption and desorption therein are used. Specifically, a waste gas containing a gaseous hydrocarbon is passed through one of the adsorbers to cause the adsorbent to adsorb the gaseous hydrocarbon and discharge the waste gas containing substantially no gaseous hydrocarbon into the air. During this operation, the other adsorber is used

as a desorber in such a manner that the gaseous hydrocarbon which has been adsorbed on the adsorbent is separated from the adsorbent layer by suction with a vacuum pump, and the gaseous hydrocarbon is recovered from the separated effluent purge gas. The adsorbent used here is not particularly limited, and examples thereof include active carbons, zeolites, and hydrophobized silica gels. Among these, hydrophobized silica gels are preferred because they are noncombustible, inexpensive, and easily available.

As described above, the present invention provides a method for adsorptively recovering a gaseous hydrocarbon contained in a waste gas which comprises: (A) cooling a desorbed gas to ordinary temperature, returning the resultant uncondensed gas containing a gaseous hydrocarbon to the inlet of an adsorber, mixing the uncondensed gas with a gas to be treated to heighten the concentration of the gaseous hydrocarbon in the gas to be treated, and sending the resultant mixture to the adsorber to conduct an adsorption step; (B) subsequently yielding a desorbed gas containing the gaseous hydrocarbon in a higher concentration than a desorbed gas to be obtained when the gas to be treated is treated alone; repeating (A) and (B) above to thereby condense a part of the hydrocarbon contained in the desorbed gas by

cooling to ordinary temperature; and recovering the condensed hydrocarbon.

In the desorption step according to the present invention, the gaseous hydrocarbon adsorbed on the adsorbent layer is first separated from the adsorbent layer by evacuation with a vacuum pump. Examples of the vacuum pump include liquid-ring vacuum pumps, complete-dry vacuum pumps, and the like. When the hydrocarbon recovered is reused, complete-dry vacuum pumps are preferred. The degree of vacuum is not particularly limited, but is preferably from 25 to 100 mmHg. During the desorption, either a part of the treated clean gas discharged from the adsorption-step adsorption column or air is introduced as a purge gas into the desorption-step column. Although the amount of the purge gas is not particularly limited, the actual flow rate thereof is preferably up to 130% based on the amount of the gas being treated. The smaller the amount of the purge gas, the higher the hydrocarbon concentration in the desorbed gas and the easier the cooling condensation. In addition, smaller purge gas amounts necessitate a smaller-capacity vacuum pump and a smaller power. However, smaller purge gas amounts result in a reduced degree of regeneration of the adsorbent. The

relationship between the purge gas and the waste gas can be represented by the following equation.

$$P = \alpha \times F \times (PL/PH)$$

P: purge gas amount, Nm^3/h

F: waste gas amount, Nm^3/h

α: purging coefficient

PL: pressure for regeneration

PH: pressure for adsorption

When the type of column constitution used for an adsorption method in the present invention is the three-column type composed of a first column for adsorption and a second and third column for desorption, it is preferred to pass a purge gas for a desorption step so that it flows serially and successively through the second column, the third column, and a vacuum pump in this order. In the case of the two-column type composed of one column for adsorption and one column for desorption, the desorption period is equal to the adsorption period, and a purge gas in an amount necessary for desorption should be fed/sucked within that period. In contrast, in the above three-column type, the desorption period can be up to two times the adsorption period and, hence, the amount of a purge gas can be as small as about 50 to 60% of that necessary in the two-column type. Furthermore, even when a purge gas

is passed in parallel through the first desorption-step column (the above second column) and the second desorption-step column (the above third column), the amount to be sucked is equal to that in the two-column type. Moreover, when a purge gas is passed serially as in the above, the purge gas discharged from the column which came into a desorption step earlier (the above second column) can be sufficiently usable for regeneration in the column which came into a desorption step later (the above third column) because it has a low hydrocarbon content. In the next stage, the first desorption-step column (the above second column) comes into an adsorption step, while the second desorption-step column (the above third column) becomes a first desorption-step column. On the other hand, the first adsorption-step column becomes a second desorption-step column.

Next, the desorbed gas is cooled to ordinary temperature. Although the ordinary temperature is not particularly limited, it is a temperature in the range of about from 10 to 30°C, preferably about 20°C. Although means for cooling are not particularly limited, it is preferred to use a cooler employing cooling water. Initially, no liquefaction occurs upon cooling to ordinary temperature because the desorbed gas is thin.

All the gas is hence returned as an uncondensed gas to the inlet of the adsorber and mixed with a gas to be treated. As a result, a mixed gas containing the gaseous hydrocarbon in a higher concentration than the initial value is introduced into the adsorber.

Subsequently, an adsorption step is conducted, followed by a gas desorption step again. The resultant desorbed gas contains the gaseous hydrocarbon in a higher concentration than a desorbed gas to be obtained when the gas to be treated is treated alone. By repeating the above operation, the concentration of the gaseous hydrocarbon in the desorbed gas gradually increases and, eventually, part of the hydrocarbon contained in the desorbed gas comes to condense upon cooling to ordinary temperature. This partial condensation of the hydrocarbon in the desorbed gas by cooling to ordinary temperature can occur when the partial pressure of the gaseous hydrocarbon in the effluent purge gas is the saturation vapor pressure of the hydrocarbon or more. The excess hydrocarbon which corresponds to the part beyond the saturation vapor pressure condenses, and a gas containing the uncondensed hydrocarbon in an amount corresponding to the saturation vapor pressure is returned to the inlet of the adsorber and mixed with the gas to be treated. For example,

since toluene has a saturation vapor pressure at 20°C of 22 mmHg (2.9 vol%), condensation begins at the time when the partial pressure of the hydrocarbon in an effluent purge gas exceeds 22 mmHg and a gas having a concentration of 2.9 vol% is returned to the inlet of the absorber.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows a flow sheet illustrating, as a mode of carrying out the present invention, a method for recovering a gaseous hydrocarbon contained in a waste gas.

BEST MODE FOR CARRYING OUT THE INVENTION

Specific modes for carrying out the present invention will be explained below in detail by reference to Examples. These Examples are intended to illustrate the present invention and should not be construed as limiting the invention. Consequently, the operation of an industrial apparatus for the PSA of VOCs which employs an adsorbent according to the present invention should not be construed as being limited by the conditions in the following Examples.

The porosity characteristics, hydrophobicity, and VOC-adsorbing ability of each of the sample adsorbents

obtained in the Examples and Comparative Examples were evaluated by the following measuring methods and evaluation methods.

Methods for Measuring Porosity Characteristics including Specific Surface Area, Pore Volume, and Average Pore Diameter

Porosity characteristics of a raw adsorbent material (hereinafter referred to as "raw-material properties") and porosity characteristics of an adsorbent obtained through a hydrophobizing treatment (hereinafter referred to as "adsorbent properties") were determined with an automatic surface area/pore diameter measuring apparatus (Belsorp28, manufactured by Bel-Japan Corp.) using high-purity N_2 (Takachiho Kagaku; research grade) as probe molecules. In determining porosity characteristics, the sample adsorbent and the raw adsorbent material were subjected to vacuum heat treatment as a pretreatment prior to the measurements of specific surface area and pore diameter, before the desired properties were then determined.

In the vacuum heat treatment of each sample, about 200 mg of the sample was placed in a sample tube made of glass, heated from room temperature to 350°C at a heating rate of 6 °C/min while maintaining a vacuum of

from 10^{-1} to 10^{-2} mmHg, and held at that temperature for 3 hours. Thereafter, the sample was cooled to room temperature at a cooling rate of 5 °C/min while maintaining a pressure of ordinary pressure + 5 mmHg with high-purity helium gas to obtain a sample to be subjected to measurements. The sample obtained was accurately weighed and subjected to the measurements of porosity characteristics.

In the porosity characteristics measurements, an automatic Dewar vessel having a liquefied-nitrogen autofeeder was used to keep the sample at the liquefied-nitrogen temperature (-196°C), and the dead volume was measured three or more times with high-purity helium. Subsequently, the vessel was evacuated and probe molecules (nitrogen) were then introduced to determine the specific surface area by the BET method. A desorption measurement was then conducted to thereby determine the average pore diameter.

Method for Evaluating Hydrophobicity of Adsorbent

The equilibrium water vapor adsorption of an adsorbent was measured at a temperature of 20°C and a pressure of 2 mmHg in order to evaluate the hydrophobicity of the adsorbent.

Prior to a measurement for determining hydrophobicity, a sample adsorbent was subjected to the following vacuum heat treatment as a pretreatment. Namely, about 100 mg of the sample was placed in a sample tube made of glass, heated from room temperature to 350°C at a heating rate of 6 °C/min while maintaining a vacuum of from 10^{-1} to 10^{-2} mmHg, and held at that temperature for 1 hour. Subsequently, the sample was cooled to room temperature at a cooling rate of 5 °C/min to obtain a sample adsorbent. The sample adsorbent obtained was accurately weighed and subjected to the measurement.

Water for use as a water vapor source was prepared in the following manner. In a sump made of glass was placed 50 ml of ion-exchanged water. This water was bubbled with a vacuum line, and dissolved gases were released from the water while evacuating the sump at about 10^{-2} mmHg and carefully cooling the bottom of the sump with a dry ice-methanol refrigerant to freeze the water. Subsequently, the ice was melted by heating. The above treatment was repeated until the water came to release no dissolved gas. Thus, purified water was obtained.

For measuring the equilibrium adsorption, a high-precision vapor adsorption measuring apparatus

(Belsorp18, manufactured by Bel-Japan Corp.) was used. In a thermostatic air chamber, the sump containing the purified water was held at 50°C ± 1°C and the water vapor in a saturation state generating from the sump was introduced into a reservoir made of glass (capacity, 150 ml) held at 50°C ± 1°C. Furthermore, water vapor was gradually introduced from the reservoir through an automatic flow regulating valve into an adsorption tube made of glass in which only the part containing the sample adsorbent was held at 20°C ± 0.5°C, and this introduction was continued until an equilibrium pressure of 2 mmHg was reached.

At the time when the equilibrium pressure of 2 mmHg was reached, i.e., when the pressure fluctuations for 10 minutes had reduced to within 0.1 mmHg, the amount of water introduced was determined from the pressure measured with a capacitance manometer and from the inner volume of the system. This water amount was taken as the equilibrium adsorption. The equilibrium adsorption per weight of the adsorbent was further calculated from the sample weight after the pretreatment. Adsorbents having smaller equilibrium adsorptions can be regarded as more hydrophobic.

In order to evaluate the resistance of an adsorbent to cracking by water as a property indicating

hydrophobicity, the sample adsorbent was immersed in 20°C water and examined for cracking after the lapse of two weeks.

The value obtained by the above hydrophobicity evaluation method is intended to be used for comparative evaluation of adsorbents as a mere measure indicating the degree of hydrophobicity of the adsorbent. It does not mean that the sample adsorbent in a PSA process actually adsorbs such an amount of water.

Method for Evaluating VOC-Adsorbing Ability of Adsorbent

In order to evaluate the VOC-adsorbing ability of a sample adsorbent, the reversible adsorption of a VOC was determined in the following manner. Namely, an isopentane/water vapor/air mixed gas having a total pressure of 760 mmHg, an i-C_5 partial pressure of 300 mmHg, a water vapor partial pressure of 10 mmHg, with the remainder being dry air was adsorbed onto the sample adsorbent at 20°C. Subsequently, the reversible isopentane adsorption was determined 5 minutes thereafter. This adsorption value was taken as the reversible VOC adsorption.

Prior to the measurement, the sample adsorbent was subjected to the following vacuum heat treatment as a pretreatment. In the vacuum heat treatment, about 100 mg of the sample was first placed in a sample tube,

heated from room temperature to 350°C at a heating rate of 6 °C/min while maintaining a vacuum of 10^{-1} to 10^{-2} mmHg, and held at that temperature for 1 hour. Subsequently, the sample was cooled to room temperature at a cooling rate of 5 °C/min to obtain a sample adsorbent. For determining the VOC-adsorbing ability, a necessary amount was precisely weighed out of the sample adsorbent and subjected to the measurement.

The isopentane to be used in the measurement was purified in the following manner. First, the isopentane (Tokyo Kasei Kogyo; special grade reagent) was placed in a sump and bubbled with a vacuum line. Thereafter, the sump was evacuated at a pressure on the order of 10^{-2} mmHg while releasing dissolved gases and carefully contacting the surface of liquefied nitrogen placed in a Dewar vessel to the bottom of the sump to cool and solidify the isopentane. Subsequently, the isopentane was melted by heating. This operation was repeated until the isopentane came to release no dissolved gas. Thus, the isopentane was purified.

Water for use as a water vapor source was purified in the same manner as in the evaluation of hydrophobicity.

Before the measurement, the purified water and isopentane were placed in respective sumps and held at a

constant temperature of 50°C ± 1°C in a thermostatic chamber.

First, the water vapor in a saturation state generating from one of the sumps was introduced, until a pressure of 30 mmHg, into a reservoir made of glass (capacity, 150 ml) kept at a temperature of 50°C ± 1°C. Furthermore, water vapor was gradually introduced from the reservoir through an automatic flow regulating valve into an adsorption tube made of glass in which only the part containing the sample adsorbent was held at 20°C ± 0.5°C, and this introduction was continued until an equilibrium pressure of 10 mmHg was reached. Subsequently, the water adsorption at the time when the equilibrium pressure of 10 mmHg was reached was determined from the pressure measured with a capacitance manometer and from the inner volume of the system.

Subsequently, the isopentane vapor generating from the other sump was introduced, until a pressure of 540 mmHg, into a reservoir made of glass (capacity, 150 ml) kept at a temperature of 50°C ± 1°C. Furthermore, isopentane vapor was gradually introduced from the reservoir through an automatic flow regulating valve into the adsorption tube made of glass in which only the part containing the sample adsorbent was held at 20°C ±

0.5°C, and this introduction was continued until an equilibrium pressure of 540 mmHg was reached.

The adsorbed amount as measured at the time when the pressure fluctuations for 10 minutes reached to within 0.1 mmHg was taken as the equilibrium adsorption. The amount of isopentane adsorbed was determined from pressure changes determined with a capacitance manometer and from the inner volume of the system, and the adsorbed amount per weight of the adsorbent was calculated from the sample weight after the pretreatment.

Alternatively, the following procedure was conducted prior to the measurement. First, water vapor was introduced from one of the sumps into a reservoir made of glass (150 ml) in an amount of 10 mmHg. Subsequently, isopentane vapor was introduced from the other sump into the reservoir made of glass in an amount of 300 mmHg to prepare a water/isopentane mixed gas having a total pressure of 310 mmHg. Thereafter, dry air was introduced into the reservoir made of glass to adjust the total pressure to 825 mmHg. The pressure was measured with a capacitance manometer, while the residual isopentane after adsorption was determined by the absolute calibration method using a gas chromatograph equipped with a flame ionization detector (FID-GC).

The isopentane/water/air mixed gas was gradually introduced through an automatic flow regulating valve into an adsorption tube made of glass in which only the sample part containing the sample adsorbent was held at 20°C (±0.5°C). The isopentane adsorption was determined at each of an equilibrium pressure of 760 mmHg and an equilibrium pressure of 20 mmHg. Pressure swinging between 760 mmHg and 20 mmHg was repeated three times, and the reversible isopentane adsorption (calculated for standard state (stp)) was determined from each resultant difference. These adsorption values were averaged, and this average was taken as the found value. Adsorbents having larger reversible isopentane adsorptions can be regarded as having higher VOC-adsorbing abilities.

For measuring the water vapor adsorption and VOC adsorption, a high-precision vapor amount measuring apparatus (Belsorp18, manufactured by Bel-Japan Corp.) was used and the flow regulating valve and the like were controlled on-line by means of a personal computer (PC9821, manufactured by NEC Corp.).

The above procedure for determining reversible isopentane adsorption was conducted on the supposition of a PSA process. Determining the reversible VOC adsorptions of adsorbents is thought to be effective in making comparative evaluation of the adsorbent

performances to be shown in an actual process. Isopentane was selected as a representative gas of VOCs. Although isopentane differs from other VOCs in absolute adsorption, use of the gas poses no problem in the comparative evaluation of adsorbents.

The adsorbents according to the present invention are adsorbents capable of selectively and efficiently adsorbing low-concentration VOCs present in the air around gas stations, oil tank stations, and the like, i.e., VOCs mixed with air to some degree. In the adsorptive recovery of such low-concentration VOCs, a problem is the influence of water contained in the air. The problem is that upon adsorption of water, the VOC-adsorbing ability may decrease. In other words, an excellent adsorbent for low-concentration VOCs is an adsorbent which is less influenced by water.

When water coexists with a VOC, an adsorbent usually preferentially adsorbs water and hence the VOC-adsorbing ability of the adsorbent decreases. In this evaluation method, an adsorbent is caused to first adsorb water and then adsorb a VOC to evaluate the adsorbing ability thereof. This means that the adsorbent whose VOC-adsorbing ability is being evaluated is in a water-rich state, i.e., in a state similar to a state in which a VOC is present in a low concentration.

In other words, an adsorbent which has adsorbed water beforehand as in this evaluation method is regarded as present in a low-concentration VOC atmosphere or under severer conditions. Therefore, that an adsorbent can adsorb a large amount of a VOC even after adsorption of water correlates in a high probability with that the adsorbent is excellent in the ability to adsorb the low-concentration VOC.

Method for Determining VOC Selectivity of Adsorbent

The equilibrium adsorption of water vapor on an adsorbent (ml/g (stp)) is measured at a pressure of 2 mmHg and a temperature of 20°C by the method used for measuring equilibrium water vapor adsorption as described in the Method for Evaluating Hydrophobicity of Adsorbent.

The equilibrium adsorption of a volatile organic compound on an adsorbent (ml/g (stp)) is measured at a temperature of 20°C and a pressure which is one-tenth the saturation vapor pressure of the volatile organic compound at 20°C. This measurement is made in the following manner.

The organic compound to be used for the measurement is purified beforehand. As an example, isopentane is used. First, isopentane as a special

grade reagent is placed in a sump and bubbled with a vacuum line. Thereafter, dissolved gases are released while evacuating the sump at a vacuum on the order of 10^{-2} mmHg and carefully contacting the surface of liquefied nitrogen placed in a Dewar vessel to the bottom of the sump to cool and solidify the isopentane. Subsequently, the solidified isopentane is melted by heating. This operation is repeated until the isopentane come to release no dissolved gas. Thus, the isopentane was degassed and purified. In the case of a volatile organic compound less apt to solidify at the liquefied-nitrogen temperature, a molecular sieve or the like which has been cooled beforehand to around the liquefied-nitrogen temperature is used to adsorb the volatile organic compound thereonto and is then heated, and the gas which is released from the molecular sieve first is collected in a gas reservoir.

The vapor of the isopentane thus degassed and purified was introduced, until about 540 mmHg, into a reservoir made of glass (capacity, 150 ml) held at 50°C ± 1°C. Furthermore, isopentane vapor was introduced from the reservoir into an adsorption tube made of glass in which the reservoir part containing the sample adsorbent was held at 20°C ± 0.5°C. The adsorbed amount was measured at the time when the pressure fluctuations

for 10 minutes at a temperature of 20°C and a pressure one-tenth the saturation vapor pressure of isopentane at a temperature of 20°C and the pressure fluctuations for 10 minutes at a pressure one-tenth the vapor pressure at 1 atm reached to 0.02 mmHg or less. This adsorbed amount (equilibrium adsorption) was taken as the equilibrium adsorption of isopentane (ml/g (stp)) at 20°C and a pressure one-tenth the saturation vapor pressure of isopentane at 20°C.

In the above explanations, isopentane was used as an example of volatile organic compounds. However, the volatile organic compounds should not be construed as being limited to isopentane.

Next, a mode of carrying out the present invention is explained by reference to Fig. 1. Fig. 1 is a flow sheet illustrating, as a mode of carrying out the present invention, a method for recovering a gaseous hydrocarbon contained in a waste gas. This method employs a fixed bed PSA process. In the figure, 2a denotes an adsorption column, 2b a desorption column, 3 a vacuum pump, 4 a cooler, 5 a condensate reservoir, 6 a recovered-oil tank, 7 an electromagnetic valve, P a pressure gauge, T a thermometer, F a flow meter, and L a level gauge. As shown in Fig. 1, a hydrocarbon-containing gas to be treated is sent to the adsorption

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column 2a (to the adsorption column 2b after switching to a desorption step) through a blower omitted in the figure. The adsorption columns 2a and 2b are operated while switching the operation mode between an adsorption step and a desorption step at switching intervals of from 3 to 10 minutes.

After completion of an adsorption step, a purge gas (e.g., air) is introduced into the adsorption column 2a or 2b and the vacuum pump 3 is operated for suction to thereby desorb the gaseous hydrocarbon adsorbed on the adsorbent. The resultant desorbed gas containing the VOC in a higher concentration is sent to the cooler 4 which cools the desorbed gas to a temperature of about 20°C. The gas remaining uncondensed (initially, the whole desorbed gas) is returned to the inlet of the adsorption column 2a or 2b. The waste gas mixed with the uncondensed gas sent to the adsorption column 2a or 2b therefore has a higher concentration. The above procedure is repeated. As a result, part of the hydrocarbon contained in the desorbed gas eventually comes to condense upon cooling to ordinary temperature. The condensed hydrocarbon is sent via the condensate reservoir 5 to the recovered-oil tank 6 and recovered.

According to the above method shown as a mode of carrying out the present invention, the concentration of

a gaseous hydrocarbon in a desorbed gas can be heightened by a simple process and this makes hydrocarbon recovery possible through cooling to ordinary temperature. Therefore, there is no need of installing a chilling unit for cooling to, e.g., 5°C or less and the method is extremely advantageous in both equipment cost and operation cost. Furthermore, since the recovery method in the mode of carrying out the present invention is applicable to a wide range of solvent-containing effluent gases ranging from low-concentration to high-concentration ones, industrial utilization thereof is of great value.

The present invention should not be construed as being limited to the above mode. For example, the adsorption column which has undergone an adsorption step may be heated to a safe temperature with a heat exchanger for heating. This necessitates a smaller purge gas amount and a vacuum pump having a smaller capacity. Furthermore, since the adsorbed amount in the recovery method of the present invention is almost proportional to the partial pressure of the hydrocarbon solvent in a low-concentration range, the need of increasing the adsorbent amount is slight.

Specific experimental results will be shown below.

EXAMPLE 1

A silica gel powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 600 m^2/g, 0.40 ml/g, and 2.5 nm, respectively, was formed by pelletizing into cylindrical pellets of 3.2 mm (diameter) by 3 mm (height). Subsequently, the pellets were heated with a muffle furnace from room temperature to 550°C at a heating rate of 1 °C/min and then held at the temperature of 550°C for 5 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 1.

The sample adsorbent of Example 1 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 570 m^2/g, a pore volume of 0.38 ml/g, and an average pore diameter of 2.5 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 5% based on the raw silica gel powder. It had a saturation water vapor adsorption at 20°C and 2 mmHg of 9.8 ml/g (stp), as measured by the method for evaluating hydrophobicity described above; "stp" means the standard state (standard temperature and pressure) and indicates the adsorbed amount calculated for 0°C and ordinary pressure. Even after the lapse of 2-week immersion in water, the sample adsorbent had no

cracks. The sample adsorbent had an isopentane adsorption of 3.1 ml/g (stp), as measured after equilibrium water adsorption at 20°C and 10 mmHg according to the above-described method for evaluating VOC-adsorbing ability.

The raw-material properties, conditions for hydrophobizing treatment, adsorbent properties, hydrophobicity, and VOC adsorption in Example 1 are given in Table 1 in the column "Example 1". The same applies in the following Examples 2 to 5.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5
Raw-material properties					
Specific surface area (m^2/g)	600	660	690	700	780
Pore volume (ml/g)	0.40	0.10	0.30	0.30	0.30
Average pore diameter (nm)	2.5	0.6	2.0	1.5	1.5
Hydrophobizing treatment					
Heat treatment temperature (°C)	550	600	650	700	620
Heating rate (°C/min)	1	5	10	20	15
Heat treatment period (h)	5	4	3	3	2
Adsorbent properties					
Specific surface area (m^2/g)	570	581	448	420	655
Pore volume (ml/g)	0.38	0.09	0.20	0.18	0.25
Average pore diameter (nm)	2.5	0.6	1.8	1.7	1.5
Decrease in specific surface area (%)	5	12	35	40	16
Hydrophobicity					
Water vapor adsorption (ml/g (stp)) (equilibrium adsorption at 2 mmHg, 20°C)	9.8	7.5	5.3	3.2	10.0
Cracking through immersion in water (2 weeks at 20°C)	not occurred	not occurred	not occurred	not occurred	not occurred
VOC adsorption (ml/g (stp))	3.1	4.5	4.1	3.7	5.9

EXAMPLE 2

A silica gel powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 660 m^2/g, 0.10 ml/g, and 0.6 nm, respectively, was formed by pelletizing into pellets of the same shape as in Example 1. The pellets were heated with a muffle furnace from room temperature to 600°C at a heating rate of 5 °C/min and then held at 600°C for 4 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 2.

The sample adsorbent of Example 2 had a specific surface area of 581 m^2/g, a pore volume of 0.09 ml/g, and an average pore diameter of 0.6 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 12% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 7.5 ml/g (stp) and 4.5 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had no cracks.

EXAMPLE 3

A spherical silica gel having a particle diameter of from 2 to 3 mm and having such raw-material

properties that the specific surface area, pore volume, and average pore diameter were 690 m^2/g, 0.30 ml/g, and 2.0 nm, respectively, was heated with a muffle furnace from room temperature to 650°C at a heating rate of 10 °C/min and then held at the temperature of 650°C for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Example 3.

The sample adsorbent of Example 3 had a specific surface area of 448 m^2/g, a pore volume of 0.20 ml/g, and an average pore diameter of 1.8 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 35% based on the raw spherical silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 5.3 ml/g (stp) and 4.1 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had no cracks.

EXAMPLE 4

A spherical silica gel having a particle diameter of from 2 to 3 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 700 m^2/g, 0.30 ml/g, and 1.5 nm, respectively, was heated with a muffle furnace from room temperature to 700°C at a heating rate of 20

°C/min and then held at 700°C for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Example 4.

The sample adsorbent of Example 4 had a specific surface area of 420 m^2/g, a pore volume of 0.18 ml/g, and an average pore diameter of 1.7 nm. Consequently, the sample adsorbent had a decrease ratio in specific surface area of 40% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 3.2 ml/g (stp) and 3.7 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had no cracks.

EXAMPLE 5

A spherical silica gel having a particle diameter of from 2 to 3 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 780 m^2/g, 0.30 ml/g, and 1.5 nm, respectively, was heated with a muffle furnace from room temperature to 620°C at a heating rate of 15 °C/min and then held at the temperature of 620°C for 2 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Example 5.

The sample adsorbent of Example 5 had a specific surface area of 655 m^2/g, a pore volume of 0.25 ml/g, and an average pore diameter of 1.5 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 16% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 10.0 ml/g (stp) and 5.9 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had no cracks.

COMPARATIVE EXAMPLE 1

A silica powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 450 m^2/g, 0.69 ml/g, and 6.1 nm, respectively, was formed by pelletizing into pellets of the same shape as in Example 1. The pellets were heated with a muffle furnace from room temperature to 650°C at a heating rate of 10 °C/min and then held at the temperature of 650°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Comparative Example 1.

The sample adsorbent of Comparative Example 1 had a specific surface area of 383 m^2/g, a pore volume of 0.59 ml/g, and an average pore diameter of 6.2 nm.

Consequently, the sample adsorbent had a decrease in specific surface area of 15% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 7.5 ml/g (stp) and 1.5 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had no cracks.

The raw-material properties, conditions for hydrophobizing treatment, adsorbent properties, hydrophobicity, and VOC adsorption in Comparative Example 1 are given in Table 2 in the column "Comparative Example 1". The same applies in the following Comparative Examples 2 to 6.

Table 2

	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Raw-material properties						
Specific surface area (m^2/g)	450	650	780	690	780	650
Pore volume (ml/g)	0.69	0.40	0.30	0.30	0.30	0.40
Average pore diameter (nm)	6.1	2.5	1.5	2.0	1.5	2.5
Hydrophobizing treatment						
Heat treatment temperature (°C)	650	800	520	800	520	700
Heating rate (°C/min)	10	30	0.5	10	5	30
Heat treatment period (h)	3	6	1	3	3	3
Adsorbent properties						
Specific surface area (m^2/g)	383	280	760	248	755	390
Pore volume (ml/g)	0.59	0.79	0.29	0.32	0.29	0.60
Average pore diameter (nm)	6.2	11.3	3.0	5.2	1.5	6.2
Decrease in specific surface area (%)	15	65	3	64	3	40
Hydrophobicity						
Water vapor adsorption (ml/g (stp)) (equilibrium adsorption at 2 mmHg, 20°C)	7.5	4.8	26.6	4.8	25.8	3.7
Cracking through immersion in water (2 weeks at 20°C)	not occurred	cracked	powdered	not occurred	powdered	cracked
VOC adsorption (ml/g (stp))	1.5	0.1	0.3	0.2	0.2	1.5

COMPARATIVE EXAMPLE 2

A spherical silica gel having a particle diameter of from 2 to 3 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 650 m^2/g, 0.40 ml/g, and 2.5 nm, respectively, was heated with a muffle furnace from room temperature to 800°C at a heating rate of 30 °C/min and then held at the temperature of 800°C for 6 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 2.

The sample adsorbent of Comparative Example 2 had a specific surface area of 280 m^2/g, a pore volume of 0.79 ml/g, and an average pore diameter of 11.3 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 65% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 4.8 ml/g (stp) and 0.1 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had considerably cracked.

COMPARATIVE EXAMPLE 3

A spherical silica gel having a particle diameter of from 2 to 3 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 780 m^2/g, 0.30 ml/g, and 1.5 nm, respectively, was heated with a muffle furnace from room temperature to 520°C at a heating rate of 0.5 °C/min and then held at the temperature of 520°C for 1 hour. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 3.

The sample adsorbent of Comparative Example 3 had a specific surface area of 760 m^2/g, a pore volume of 0.29 ml/g, and an average pore diameter of 3.0 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 3% based on the raw silica gel. It further had a saturation water vapor adsorption and an isopentane adsorption, as determined in the same manners as in Example 1, of 26.6 ml/g (stp) and 0.3 ml/g (stp), respectively. After the lapse of 2-week immersion in water, the sample adsorbent had powdered.

COMPARATIVE EXAMPLE 4

A spherical silica gel (diameter, 2-3 mm) having such raw-material properties that the specific surface

area, pore volume, and average pore diameter were 690 m^2/g, 0.30 ml/g, and 2.0 nm, respectively, was heated with a muffle furnace from room temperature to 800°C at a heating rate of 10 °C/min and then held at that temperature for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 4.

The sample adsorbent of Comparative Example 4 had a specific surface area of 248 m^2/g, a pore volume of 0.32 ml/g, and an average pore diameter of 5.2 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 64% based on the raw silica gel. It further had a saturation water vapor adsorption at 20°C and 2 mmHg, which indicates hydrophobicity, of 4.8 ml/g (stp). After the lapse of 2-week immersion in water, the sample adsorbent had no cracks. It had an isopentane adsorption, as measured after equilibrium water adsorption at 20°C and 10 mmHg, of 0.2 ml/g (stp).

COMPARATIVE EXAMPLE 5

A spherical silica gel having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 780 m^2/g, 0.30 ml/g, and 1.5 nm, respectively, was heated with a muffle furnace from room temperature to 520°C at a heating rate of 5

°C/min and then held at that temperature for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 5.

The sample adsorbent of Comparative Example 5 had a specific surface area of 755 m^2/g, a pore volume of 0.29 ml/g, and an average pore diameter of 1.5 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 3% based on the raw silica gel. It further had a saturation water vapor adsorption at 20°C and 2 mmHg, which indicates hydrophobicity, of 25.8 ml/g (stp). After the lapse of 2-week immersion in water, the sample adsorbent had powdered. It had an isopentane adsorption, as measured after equilibrium water adsorption at 20°C and 10 mmHg, of 0.2 ml/g (stp).

COMPARATIVE EXAMPLE 6

A spherical silica gel having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 650 m^2/g, 0.40 ml/g, and 2.5 nm, respectively, was heated with a muffle furnace from room temperature to 700°C at a heating rate of 30 °C/min and then held at that temperature for 3 hours. Thereafter, the silica gel was cooled to room

temperature to obtain a sample adsorbent of Comparative Example 6.

The sample adsorbent of Comparative Example 6 had a specific surface area of 390 m^2/g, a pore volume of 0.60 ml/g, and an average pore diameter of 6.2 nm. Consequently, the sample adsorbent had a decrease ratio in specific surface area of 40% based on the raw silica gel. It further had a saturation water vapor adsorption at 20°C and 2 mmHg, which indicates hydrophobicity, of 3.7 ml/g (stp). After the lapse of 2-week immersion in water, the sample adsorbent had cracked. It had an isopentane adsorption, as measured after equilibrium water adsorption at 20°C and 10 mmHg, of 1.5 ml/g (stp).

As can be seen from a comparison between the Examples and the Comparative Examples, the VOC adsorptions in all Examples were at least two times those in the Comparative Examples. In addition, the sample adsorbents of the Comparative Examples had powdered or cracked.

Furthermore, the sample adsorbents having a specific surface area smaller than 400 m^2/g have an exceedingly poor VOC-adsorbing ability as in Comparative Examples 1 and 2. In contrast, the adsorbents having a specific surface area larger than 700 m^2/g are apt to crack as in Comparative Example 3. Moreover, the sample

adsorbents obtained from raw silica gels having a specific surface area smaller than 600 m^2/g have an exceedingly poor VOC-adsorbing ability as in Comparative Example 1.

The adsorbent of Comparative Example 1 shows satisfactory hydrophobicity because it has undergone hydrophobizing treatment under the conditions specified in the present invention. However, it has a poor VOC-adsorbing ability because the specific surface area, pore volume, and average pore diameter thereof are outside the respective ranges specified in the present invention.

In Comparative Example 2, the silica gel suffered sintering, deformation, or the like because the conditions for hydrophobizing treatment, i.e., the heating rate and heat treatment temperature, were higher than the respective upper limits of the ranges specified in the present invention, although the raw-material properties of the raw silica gel were within the ranges specified in the present invention. As a result, the sample adsorbent has an extremely poor VOC-adsorbing ability and has cracked, although the water vapor adsorption thereof is relatively small.

The sample adsorbent of Comparative Example 3 has poor hydrophobicity and an extremely poor VOC-adsorbing

ability because the hydrophobizing treatment was insufficient due to the conditions for hydrophobizing treatment, especially the heat treatment temperature, which was below the lower limit specified in the present invention, although the raw-material properties of the raw silica gel were within the ranges specified in the present invention.

In Comparative Example 4, the hydrophobizing treatment temperature was 800°C, which is higher than the upper limit of the temperature range specified in the present invention, although the raw-material properties were the same as in Example 3. Consequently, the sample adsorbent obtained has a specific surface area smaller than the lower limit of the range specified in the present invention due to the considerably large decrease in specific surface area, although the adsorbent material is satisfactorily hydrophobized. Hence, a sufficient VOC adsorption was not obtained and the sample adsorbent was unsuitable for use as an adsorbent.

In Comparative Example 5, the hydrophobizing treatment temperature was 520°C, which is lower than the lower limit of the temperature range specified in the present invention, although the raw-material properties were the same as in Example 5. As a result, the

decrease in specific surface area was small so as to maintain the raw-material properties. However, the sample adsorbent has been insufficiently hydrophobized due to the low temperature range, has an exceedingly large water vapor adsorption, and has powdered considerably upon immersion in water. As a result, it has an exceedingly small VOC adsorption.

In Comparative Example 6, the heating rate in the hydrophobizing treatment was 30 °C/min, which is higher than the upper limit of the heating rate range specified in the present invention, although the raw-material properties were within the ranges specified in the present invention. The adsorbent is hence apt to deform. The sample adsorbent has been satisfactorily hydrophobized, when judged by the water adsorption thereof, because the heat treatment temperature was within the specific range. However, it cracked upon immersion in water because it had deformed considerably. The sample adsorbent further had an insufficient VOC adsorption and was unsuitable for use as an adsorbent.

A comparison between the results for Examples 1 to 5 given in Table 1 and the results for Comparative Examples 1 to 6 shows that hydrophobicity is effectively imparted by heating a raw material to a temperature in the range of from 550 to 700°C at a heating rate of from

1 to 20 °C/min and keeping it in that temperature range for from 2 to 5 hours.

Furthermore, by using a silica gel having raw-material properties within the ranges specified in the present invention, an adsorbent can be obtained which has satisfactory hydrophobicity, such as resistance to cracking caused by water and water repellency, and has a high VOC-adsorbing ability.

Evaluation with respect to VOC Selectivity

Sample adsorbents were examined for VOC selectivity as a factor indicating VOC-adsorbing ability. The VOC selectivities of the sample adsorbents of Examples 1 to 5 and Comparative Examples 1 to 6 were determined by the above-described method with respect to the specified VOCs as shown in Tables 3 and 4. The results shown in Tables 3 and 4 were obtained. The VOC selectivity of the sample adsorbent of Example 3 was determined with respect to three VOCs.

As a comparison between Table 3 and Table 4 shows, the sample adsorbents of Examples 1 to 5 each has a VOC selectivity of 85% or more, which is far higher than the VOC selectivities of 74% or less for the sample adsorbents of Comparative Examples 1 to 6. The test of the sample adsorbent of Example 3 has demonstrated that

the sample adsorbent of Example 3 shows almost the same selectivity to different VOCs.

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Table 3

VOC-Adsorbing Ability	Example 1	Example 2	Example 3			Example 4	Example 5
Name of adsorbate VOC	A	B	C	B	D	E	D
VOC adsorption (ml/g (stp))	56.6	43.6	48.1	35.2	36.0	37.9	57.3
VOC selectivity (%)	85.2	85.3	90.1	86.9	87.2	92.2	85.1

Name of adsorbate VOC

A: 2-propanol

B: isopentane

C: MEK

D: dichloromethane

E: ethyl acetate

Table 4

VOC-Adsorbing Ability	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Name of adsorbate VOC	E	B	F	C	D	A
VOC adsorption (ml/g (stp))	21.6	9.7	11.9	5.5	6.9	8.4
VOC selectivity (%)	74.2	66.9	30.9	53.4	21.1	69.4

Name of adsorbate VOC

A: 2-propanol

B: isopentane

C: MEK

D: dichloromethane

E: ethyl acetate

F: toluene

EXAMPLE 6

A 35 g portion of a silica gel powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 520 m^2/g, 0.70 ml/g, and 5.0 nm, respectively, was weighed out. Thereto was added 15 g of succinic acid. The resultant mixture was sufficiently dry-kneaded with an automatic mortar and then pelletized with a pelletizer into cylindrical pellets of 3 mm (diameter) by 3 mm (height).

Subsequently, the pellets were heated with a muffle furnace from room temperature to 450°C at a heating rate of 0.5 °C/min and then held at the temperature of 450°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 6.

The sample adsorbent of Example 6 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 507 m^2/g, a pore volume of 0.6 ml/g, and an average pore diameter of 5.2 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 2.5% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 5.9 ml/g (stp) at a temperature of 20°C and a water vapor pressure of 2 mmHg as measured according to the method for evaluating hydrophobicity

described above; "stp" means the standard state (standard temperature and pressure) and indicates the adsorbed amount calculated for 0°C and ordinary pressure. Even after the lapse of 2-week immersion in water, the sample adsorbent had no cracks. The sample adsorbent was examined for VOC-adsorbing ability according to the above-described method for evaluating VOC-adsorbing ability. As a result, the reversible isopentane adsorption thereof at 20°C (δq) was found to be 8.0 ml/g (stp).

The raw-material properties, conditions for hydrophobizing treatment, adsorbent properties, hydrophobicity, and VOC adsorption in Example 6 are given in Table 5 in the column "Example 6". The same applies in the following Examples 7 to 11 and Comparative Examples 7 to 10.

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Table 5

	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10
Silica properties										
Specific surface area (m^2/g)	520	550	690	690	780	780	520	780	690	550
Pore volume (ml/g (stp))	0.7	0.6	0.3	0.3	0.3	0.3	0.7	0.3	0.3	0.6
Average pore diameter (nm)	5.0	4.3	2.0	2.0	1.7	1.7	5.0	1.7	2.0	4.3
Hydrophobizing treatment										
Second ingredient	succinic acid	tartaric acid	PA	CMC	PVA	CMC	-	-	CMC	PVA
Amount of second ingredient (wt%)	30	20	25	5	2	10	-	-	5	2
Heat treatment temperature (°C)	450	400	500	680	750	630	400	750	300	800
Average heating rate (°C/min)	0.5	1.5	3	7	10	20	25	10	3	20
Heat treatment period (h)	3	3	3	3	3	3	1	1	3	3
Adsorbent properties										
Specific surface area (m^2/g)	507	540	670	517	450	597	500	242	680	229
Pore volume (ml/g (stp))	0.6	0.6	0.4	0.3	0.3	0.3	0.7	0.5	0.3	0.4
Average pore diameter (nm)	5.2	4.5	2.1	2.3	2.3	2.0	5.2	8.2	2.0	7.1
Decrease in specific surface area (%)	2.5	1.8	2.9	25.1	42.3	23.5	3.8	68.9	1.4	58.4
Hydrophobicity										
Water vapor adsorption (ml/g) (equilibrium adsorption at 2 mmHg, 20°C)	5.9	7.5	9.7	7.3	8.4	9.4	25.1	4.6	18.0	4.5
Cracking upon immersion in water	none	none	none	none	none	none	cracked	none	cracked	none
Reversible iso-C_5H_{12} adsorption	8.0	8.5	10.5	8.2	7.1	9.4	8.0	3.1	11.0	3.5

EXAMPLE 7

A 40 g portion of a spherical silica gel having an average particle diameter of 2.5 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 550 m^2/g, 0.60 ml/g, and 4.3 nm, respectively, was weighed out. The weighed silica gel was heated at a temperature of 400°C for 60 minutes in air and then allowed to cool to room temperature.

In water was dissolved 10 g of tartaric acid to prepare 50 ml of an aqueous tartaric acid solution. In the whole aqueous tartaric acid solution prepared was immersed the 40 g of spherical silica gel. This silica gel in the immersed state was allowed to stand at room temperature for 1 hour to impregnate the same. The impregnated silica gel was placed in a thermostatic drying chamber kept at about 100°C to remove the water, subsequently heated to 400°C at an average heating rate of 1.5 °C/min, and then held at the temperature of 400°C for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Example 7.

The sample adsorbent of Example 7 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 540 m^2/g, a pore volume

of 0.6 ml/g, and an average pore diameter of 4.5 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 1.8% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 7.5 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 8.5 ml/g (stp).

EXAMPLE 8

A 40 g portion of a spherical silica gel having an average particle diameter of 2.5 mm and having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 690 m^2/g, 0.30 ml/g, and 2.0 nm, respectively, was weighed out. The weighed silica gel was heated at a temperature of 500°C for 60 minutes in air and then allowed to cool to room temperature.

In water was dissolved 13.3 g of propionaldehyde (PA) to prepare 50 ml of an aqueous propionaldehyde solution. In the whole aqueous propionaldehyde solution prepared was immersed the 40 g of spherical silica gel. This silica gel in the immersed state was allowed to stand at room temperature for 1 hour to impregnate the same. The impregnated silica gel was placed in a thermostatic drying chamber kept at about 100°C to

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remove the water, subsequently heated to 500°C at an average heating rate of 3 °C/min, and then held at the temperature of 500°C for 3 hours. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Example 8.

The sample adsorbent of Example 8 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 670 m^2/g, a pore volume of 0.4 ml/g, and an average pore diameter of 2.1 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 2.9% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 9.7 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 10.5 ml/g (stp).

EXAMPLE 9

A 47.5 g portion of a silica gel powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 690 m^2/g, 0.3 ml/g, and 2.0 nm, respectively, was weighed out. Thereto was added 2.5 g of carboxymethyl cellulose (CMC). The resultant mixture was sufficiently dry-kneaded with an automatic mortar and then pelletized

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with a pelletizer into cylindrical pellets of 3 mm (diameter) by 3 mm (height).

Subsequently, the pellets were heated with a muffle furnace from room temperature to 680°C at a heating rate of 7 °C/min and then held at the temperature of 680°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 9.

The sample adsorbent of Example 9 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 517 m^2/g, a pore volume of 0.3 ml/g, and an average pore diameter of 2.3 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 25.1% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 7.3 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 8.2 ml/g (stp).

EXAMPLE 10

A 49 g portion of a silica gel powder having such raw-material properties that the specific surface area, pore volume, and average pore diameter were 780 m^2/g, 0.3 ml/g, and 1.7 nm, respectively, was weighed out. Thereto was added 1.0 g of poly(vinyl alcohol) (PVA),

followed by about 50 ml of water. The resultant mixture was sufficiently wet-kneaded with an automatic mortar, subsequently dried in an air bath, and then pelletized with a pelletizer into cylindrical pellets of 3 mm (diameter) by 3 mm (height).

Subsequently, the pellets were heated with a muffle furnace from room temperature to 750°C at a heating rate of 10 °C/min and then held at the temperature of 750°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 10.

The sample adsorbent of Example 10 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 450 m^2/g, a pore volume of 0.3 ml/g, and an average pore diameter of 2.3 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 42.3% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 8.4 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 7.1 ml/g (stp).

EXAMPLE 11

A 45 g portion of a silica gel powder having the same raw-material properties as in Example 10 was

weighed out. Thereto was added 5 g of carboxymethyl cellulose (CMC). The resultant mixture was sufficiently dry-kneaded with an automatic mortar and then pelletized with a pelletizer into cylindrical pellets of 3 mm (diameter) by 3 mm (height).

Subsequently, the pellets were heated with a muffle furnace from room temperature to 630°C at a heating rate of 20 °C/min and then held at the temperature of 630°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Example 11.

The sample adsorbent of Example 11 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 597 m^2/g, a pore volume of 0.3 ml/g, and an average pore diameter of 2.0 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 23.5% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 9.4 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 9.4 ml/g (stp).

COMPARATIVE EXAMPLE 7

A spherical silica gel having an average particle diameter of 2.5 mm and having the same raw-material

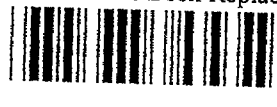
properties as in Example 6 was heated to 400°C in air at an average heating rate of 25 °C/min and then held at the temperature of 400°C for 1 hour. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 7.

The sample adsorbent of Comparative Example 7 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 500 m^2/g, a pore volume of 0.7 ml/g, and an average pore diameter of 5.2 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 3.8% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 25.1 ml/g (stp) and had cracked after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 8.0 ml/g (stp).

COMPARATIVE EXAMPLE 8

A spherical silica gel having an average particle diameter of 2.5 mm and having the same raw-material properties as in Examples 10 and 11 was heated to 750°C in air at an average heating rate of 10 °C/min and then held at the temperature of 750°C for 1 hour. Thereafter, the silica gel was cooled to room temperature to obtain a sample adsorbent of Comparative Example 8.

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The sample adsorbent of Comparative Example 8 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 242 m^2/g, a pore volume of 0.5 ml/g, and an average pore diameter of 8.2 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 68.9% based on the raw silica gel powder. It had an equilibrium water vapor adsorption of 4.6 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 3.1 ml/g (stp).

COMPARATIVE EXAMPLE 9

A sample adsorbent of Comparative Example 9 was obtained in the same manner as in Example 9, except that pellets obtained in the same manner as in Example 9 were heated with a muffle furnace from room temperature to 300°C at a heating rate of 3 °C/min and then held at the temperature of 300°C.

The sample adsorbent of Comparative Example 9 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 680 m^2/g, a pore volume of 0.3 ml/g, and an average pore diameter of 2.0 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 1.4% based on the

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raw silica gel powder. It had an equilibrium water vapor adsorption of 18.0 ml/g (stp) and had cracked after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 11.0 ml/g (stp).

COMPARATIVE EXAMPLE 10

A 49 g portion of a spherical silica gel having the same raw-material properties as in Example 7 was weighed out. Thereto was added 1.0 g of poly(vinyl alcohol) (PVA). The resultant mixture was sufficiently dry-kneaded with an automatic mortar and then pelletized with a pelletizer into cylindrical pellets of 3 mm (diameter) by 3 mm (height).

Subsequently, the pellets were heated with a muffle furnace from room temperature to 800°C at a heating rate of 20 °C/min and then held at the temperature of 800°C for 3 hours. Thereafter, the pellets were cooled to room temperature to obtain a sample adsorbent of Comparative Example 10.

The sample adsorbent of Comparative Example 10 was examined for properties. As a result, the adsorbent was found to have a specific surface area of 229 m^2/g, a pore volume of 0.4 ml/g, and an average pore diameter of 7.1 nm. Consequently, the sample adsorbent had a decrease in specific surface area of 58.4% based on the

raw silica gel powder. It had an equilibrium water vapor adsorption of 4.5 ml/g (stp) and had no cracks even after the lapse of 2-week immersion in water. It had a reversible isopentane adsorption (δq) of 3.5 ml/g (stp).

(Evaluation of Examples 6 to 11 and Comparative Examples 7 to 10)

Generally speaking, the adsorbents of Examples 6 to 11 have a water vapor adsorption of 9.7 ml/g (stp) or smaller, do not crack upon immersion in water, and have a reversible isopentane adsorption of 5.9 ml/g (stp) or larger. The sample adsorbents of Examples 6 to 11 can hence be judged to be adsorbents suitable for the PSA of VOCs.

From the fact that the decreases in specific surface area in Examples 6 to 8 and Comparative Examples 7 and 9 are 4% or lower, it can be concluded that heat treatment at temperatures not higher than 500°C hardly impairs the raw-material properties. Namely, it can be seen that heat history is almost negligible. It is thought that by adding a second ingredient to a raw silica gel and subjecting the mixture to heat treatment in a low-temperature range of up to 500°C, a hydrophobizing effect is produced by the second

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ingredient or decomposition products (including radicals, *etc.*) of the second ingredient.

It can be seen from Examples 6 to 8 that by the addition of a second ingredient, a hydrophobizing effect can be produced through heat treatment in a low-temperature range while substantially maintaining the raw-material properties.

The reason why the decrease in specific surface area in Example 6, which is 2.5%, is higher than that in Example 2, which is 1.8%, may be that the heat treatment temperature in Example 6 is higher than in Example 7.

Example 7 is intended to demonstrate the effect of the addition of a second ingredient when a silica gel having almost the same raw-material properties as the silica gel used in Comparative Example 6 is used and heat treatment is conducted at the same low temperature of 400°C as in Comparative Example 6. The adsorbent of Example 2, in which a second ingredient was added, has a water vapor adsorption as small as about one-third (7.5 ml/g (stp)) that in Comparative Example 1 and did not crack upon immersion in water. This indicates that due to the addition of a second ingredient, hydrophobicity is imparted and the adsorbent strength is improved. The decreases in specific surface area in Example 7 and Comparative Example 7 are 1.8% and 3.8%, respectively.

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Although the difference therebetween is not large, a significant effect of diminishing the decrease in specific surface area by the addition of a second ingredient is observed.

In Example 9, heat treatment was conducted at 680°C, which is close to the upper limit of the temperature range. It is thought that heat shrinkage occurred as apparent from the decrease in specific surface area of 25.1%. However, in Comparative Example 8, in which a high heat treatment temperature was used likewise, the decrease in specific surface area is as high as about 69% because of the absence of any second ingredient during heat treatment, and the adsorbent has an enlarged average pore diameter and hence a reduced content of micropores. A composition between Example 9 and Comparative Example 8 shows that when heat treatment is conducted in a high-temperature range exceeding 500°C, the second ingredient is highly effective in maintaining raw-material properties.

In Example 11, a second ingredient was added to a raw silica gel having the same raw-material properties as in Example 10 and heat treatment was conducted at a preferred temperature. The adsorbent of Example 11 has a smaller decrease in specific surface area than in

Example 10 and is also excellent in VOC-adsorbing ability and hydrophobicity.

In Comparative Examples 7 and 10, in which the reversible isopentane adsorptions are large, the water vapor adsorptions are at least two times those in the Examples. On the other hand, in Comparative Examples 8 and 10, in which the water vapor adsorptions are small, the water vapor adsorptions are considerably smaller than in the Examples.

Although the adsorbent of Comparative Example 10 has been hydrophobized because it contains a second ingredient, it has a decrease in specific surface area as large as 58.4% and a small reversible VOC adsorption due to the too high heat treatment temperature and the resultant considerable shrinkage of the silica gel. However, a comparison with the adsorbent of Comparative Example 8, which contains no second ingredient and has a decrease in specific surface area of 68.9%, shows that the addition of a second ingredient in Comparative Example 10 is effective.

The above results will be further discussed in detail while comparing the Examples with the Comparative Examples.

Comparative Example 7 and Example 6 are equal to each other in the raw-material properties of the silica

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gel, although they differ in the shape of the silica gel and in heat treatment conditions. The adsorbent of Comparative Example 7, which contains no second ingredient, has a water vapor adsorption about 4 times that in Example 6. The decreases in specific surface area in Comparative Example 7 and Example 6 are 3.8% and 2.5%, respectively. The adsorbent of Comparative Example 7, containing no second ingredient, cracked upon immersion in water. In Comparative Example 7, the considerable powdering is thought to have been caused by the deformation of the adsorbent, resulting from the too high average heating rate of 25 °C/min, coupled with the large water absorption. The above comparison between Comparative Example 7 and Example 6 demonstrates the effectiveness of the addition of a second ingredient.

In both Comparative Example 8 and Example 10, a heat treatment temperature of 750°C was used, which is on the upper limit. These two are equal in the raw-material properties of the silica gel although different in the shape of the silica gel. Although these two differ also in the temperature keeping time in the heat treatment step, the important difference therebetween is that no second ingredient is added in Comparative Example 8.

The decreases in specific surface area in Example 10 and Comparative Example 8 are 42.3% and a value close to 69%, respectively. The average pore diameter in Example 10 is 2.3 nm, which is slightly larger than the average pore diameter of the raw silica gel, i.e., 1.7 nm. In contrast, the average pore diameter in Comparative Example 8 is 8.2 nm, which is far larger than that. Furthermore, the adsorbent of Comparative Example 8 has a water vapor adsorption about one-half that in Example 10 but has a reversible isopentane adsorption about one-third that in Example 10. It can be seen from these results that the addition of a second ingredient is highly effective in maintaining properties when burning is conducted in a high-temperature range.

Comparative Example 9 and Example 9 are equal to each other in the raw-material properties of the silica gel and the kind and addition amount of the second ingredient, but considerably differ in the temperature for the heat treatment step. Specifically, the heat treatment temperature in Comparative Example 9 is 300°C, while that in Example 9 is 750°C. Because of this, the adsorbent of Comparative Example 9 has a water vapor adsorption about 2.5 times that in Example 9. This proves that the temperature for the heat temperature step is important.

A comparison between Comparative Example 9 and Example 8 also shows the importance of the temperature for the heat treatment step. Comparative Example 9 and Example 8 are equal to each other in the raw-material properties of the silica gel and in that a second ingredient is added. These two demonstrate the influence of a difference in heat treatment temperature on adsorbents each containing a second ingredient and heated at the same average heating rate. Both adsorbents are satisfactory in reversible isopentane adsorption. However, the adsorbent of Comparative Example 9, in which heat treatment was conducted at 300°C, lower than the given heat treatment temperatures, has a water vapor adsorption as large as 18.0 ml/g (stp) and cracked upon immersion in water. This comparative adsorbent is hence unsuitable for use as an adsorbent. In contrast, the adsorbent of Example 8 is an excellent adsorbent having high hydrophobicity and a high VOC-adsorbing ability.

Comparative Example 10 and Example 7 are equal to each other in the raw-material properties of the silica gel and in that a second ingredient is added although the second ingredients differ in kind. In addition, the heating rates in the respective heat treatment steps are within the range specified in the present invention.

However, the temperatures for the respective heat treatment steps differ considerably, i.e., 800°C in Comparative Example 10 and 400°C in Example 7. Because of this, the adsorbent of Comparative Example 10 has a reversible isopentane adsorption not larger than one-half that in Example 2. This proves that the temperature for the heat treatment step is important. A comparison between Comparative Example 9 and Example 8 also shows the importance of the temperature for the heat treatment step.

As apparent from the above explanation, by adding a second ingredient to a silica gel, hydrophobicity can be imparted even through low-temperature heat treatment, and raw-material properties can be inhibited from decreasing through high-temperature heat treatment.

As a result, the raw-material property requirements for raw silica gels are less severe and there is a wider choice of raw silica gels. Hence, a more inexpensive silica gel can be used. Furthermore, since the adsorbents of the Examples have excellent hydrophobicity, they can retain over long a mechanical strength required of adsorbents. Therefore, use of the adsorbents of the Examples enables a PSA apparatus to be operated stably while maintaining a high recovery performance over long.

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Evaluation with respect to VOC Selectivity

Sample adsorbents were examined for VOC selectivity as a factor indicating VOC-adsorbing ability. The VOC selectivities of the sample adsorbents of Examples 6 to 11 and Comparative Examples 7 to 10 were determined by the above-described method with respect to the specified VOCs as shown in Table 6. The results shown in Table 6 were obtained.

As Table 6 shows, the sample adsorbents of Examples 6 to 11 each has a VOC selectivity of 85% or higher, which is far higher than the VOC selectivities of 74% or lower for the sample adsorbents of Comparative Examples 7 to 10.

Comparisons between the sample adsorbents of Example 6 and Comparative Example 10, between the sample adsorbents of Example 8 and Comparative Example 7, between the sample adsorbents of Example 9 and Comparative Example 8, and between the sample adsorbents of Example 11 and Comparative Example 9, wherein each Example uses the same VOC adsorbate as the Comparative Example compared therewith, show that the sample adsorbent of each of all these Examples, where different VOCs are used, has a VOC selectivity higher by about from 15% to 20% than that of the sample adsorbent of the compared Comparative Example.

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Table 6

	Name of adsorbate VOC	VOC adsorption (ml/g (stp))	VOC selectivity (%)
Example 6	methanol	48.6	89.2
Example 7	benzene	42.7	85.1
Example 8	dichloromethane	59.6	86.0
Example 9	MEK	71.1	90.7
Example 10	MIBK	55.1	86.8
Example 11	isopentane	58.4	86.1
Comp. Ex. 7	dichloromethane	27.1	51.9
Comp. Ex. 8	MEK	10.5	69.5
Comp. Ex. 9	isopentane	27.5	60.4
Comp. Ex. 10	methanol	13.1	74.4

It can be seen from the above that the sample adsorbents of the Examples have an exceedingly high VOC-adsorbing ability.

EXAMPLE 12

A 100 g portion of molded silica gel spheres having a surface area of 710 m^2/g, an average pore diameter of 1.5 nm, a pore volume of 0.38 ml/g, and a particle diameter of from 6 to 8 meshes was weighed out, and a 0.62 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 500°C at

a heating rate of 2 °C/min and heated at the temperature of 500°C in air for 5 hours.

The whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 350°C in a carbon monoxide atmosphere at a heating rate of 2 °C/min, and heat-treated at the temperature of 350°C for 15 hours.

Through the above treatments, a silica gel based adsorbent in which the ratio of the number of aluminum atoms in the silica gel to the number of silicon and aluminum atoms therein (hereinafter, the ratio of the number of metal atoms in a silica gel to the number of silicon and metal atoms therein is referred to simply as atom number ratio) was 1000:1 was obtained as a sample adsorbent of Example 12.

The sample adsorbent of Example 12 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 590 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.32 ml/g. It had a saturation water vapor

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adsorption as measured according to the method for evaluating hydrophobicity described above (the same applies in the following Examples and Comparative Examples) of 17.8 ml/g. It further had a reversible isopentane adsorption as measured according to the method for evaluating VOC-adsorbing ability described above (the same applies in the following Examples and Comparative Examples) of 9.1 ml/g. This adsorbent did not crack even in the above-described immersion test using distilled water.

The raw-material properties for the sample adsorbent, treatment conditions, adsorbent properties, saturation water vapor adsorption, and reversible isopentane adsorption in Example 12 are given in Table 7 in the column "Example 12". The same applies in the following Examples 13 to 20 and Comparative Examples 11 to 15.

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Table 7

	Properties of raw silica		Processing method				Adsorbent properties		Adsorbent performances		
	BET surface area (m^2/g)	Average pore diameter (nm)	Additive	Temperature for pretreatment (°C)	Si/M ratio*1 (-)	Temperature for heat treatment (°C)	BET surface area (m^2/g)	Average pore diameter (nm)	H_2O adsorption (ml/g)	Reversible $i\text{-}C_5H_{12}$ adsorption (ml/g)	Cracking upon immersion in water
Ex. 12	710	1.5	A	500	1000	350	590	1.5	17.8	9.1	none
Ex. 13	710	1.5	A	550	500	350	570	1.5	12.2	9.2	none
Ex. 14	710	1.5	B	600	1000	500	510	1.5	8.4	8.5	none
Ex. 15	710	1.5	A	680	3000	500	420	1.5	4.8	7.7	none
Ex. 16	690	1.5	A	-	500	550	550	1.5	10.5	9.0	none
Ex. 17	690	1.5	C	-	2000	500	570	1.5	16.1	8.8	none
Ex. 18	840	1.3	B	-	3000	680	460	1.2	8.8	9.5	none
Ex. 19	580	1.3	D	550	500	350	520	1.3	9.9	8.4	none
Ex. 20	560	3.6	C	600	3000	500	500	3.4	8.7	8.4	none
Comp. Ex. 11	710	1.5	-	-	-	-	710	1.5	64.1	8.9	cracked
Comp. Ex. 12	710	1.5	A	750	5000	500	290	1.5	3.9	3.5	none
Comp. Ex. 13	580	1.5	A	450	1000	200	560	1.5	28.8	8.4	cracked
Comp. Ex. 14	690	1.5	A	-	100	680	330	1.5	3.3	5.1	none
Comp. Ex. 15	430	5.6	B	-	1000	500	340	5.2	17.4	4.7	none

*1: atom number ratio; M=Al, Zr, Ti

A: $Al(NO_3)_3 \cdot 9H_2O$, B: $ZrO(NO_3)_2 \cdot 2H_2O$, C; $Ti(SO_4)_2$aq., D: $Al[CH_3CH(OH)COO]_3$

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EXAMPLE 13

A 100 g portion of the same molded silica gel as in Example 12 and a 1.24 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were weighed out.

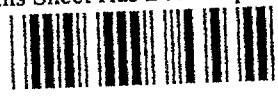
Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 550°C at a heating rate of 2 °C/min and heated at the temperature of 550°C in air for 5 hours.

The whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 350°C in air at a heating rate of 2 °C/min, and heat-treated at the temperature of 350°C for 15 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 500:1 was obtained as a sample adsorbent of Example 13.

The sample adsorbent of Example 13 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 570 m^2/g, an average pore diameter of 1.5 nm, and a pore

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volume of 0.30 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 12.2 ml/g and 9.2 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

EXAMPLE 14

A 100 g portion of the same molded silica gel as in Example 12 and a 0.45 g portion of zirconium oxynitrate dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$) were weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 600°C at a heating rate of 2 °C/min and heated at the temperature of 600°C in air for 5 hours.

The whole weighed zirconium oxynitrate dihydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 500°C under vacuum at a heating rate of 2 °C/min, and heat-treated at the temperature of 500°C for 3 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 1000:1 was obtained as a sample adsorbent of Example 14.

The sample adsorbent of Example 14 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 510 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.27 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 8.4 ml/g and 8.5 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

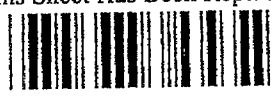
EXAMPLE 15

A 100 g portion of the same molded silica gel as in Example 12 and a 0.21 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 680°C at a heating rate of 2 °C/min and heated at the temperature of 680°C in air for 3 hours.

The whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours.

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Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 500°C in a carbon monoxide atmosphere at a heating rate of 2 °C/min, and heat-treated at the temperature of 500°C for 3 hours.

Through the above treatments, a silica gel based adsorbent having a silicon/aluminum atom number ratio of 3000:1 was obtained as a sample adsorbent of Example 15.

The sample adsorbent of Example 15 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 420 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.23 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 4.8 ml/g and 7.7 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

EXAMPLE 16

A 100 g portion of a powdery silica gel having a surface area of 690 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.38 ml/g was weighed out, and a 1.24 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was weighed out.

Subsequently, the whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water

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to prepare an aqueous solution. Thereafter, the whole aqueous solution prepared and the whole weighed powdery silica gel were wet-kneaded with an automatic mortar for 30 minutes. The mixture thus obtained through kneading was dried in an oven at 110°C for 15 hours and the resultant mixed powder was pelletized into cylindrical pellets having a diameter of 2.0 mm and a height of 3.0 mm. These moldings were heated with an electric furnace to 550°C at a heating rate of 2 °C/min and heat-treated at the temperature of 550°C in a carbon monoxide atmosphere for 5 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 500:1 was obtained as a sample adsorbent of Example 16.

The sample adsorbent of Example 16 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 550 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.29 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 10.5 ml/g and 9.0 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

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EXAMPLE 17

A 100 g portion of the same powdery silica gel as in Example 16 and a 0.50 g portion of 40% aqueous titanium sulfate solution ($Ti(SO_4)_2aq$) were weighed out.

Subsequently, the whole weighed 40% aqueous titanium sulfate solution and the whole weighed powdery silica gel were wet-kneaded with an automatic mortar for 10 minutes. The mixture thus obtained through kneading was dried in an oven at 110°C for 15 hours and the resultant mixed powder was pelletized into cylindrical pellets having a diameter of 2.0 mm and a height of 3.0 mm. These moldings were heated with an electric furnace to 500°C at a heating rate of 2 °C/min in a carbon monoxide atmosphere and heat-treated at the temperature of 500°C for 5 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 2000:1 was obtained as a sample adsorbent of Example 17.

The sample adsorbent of Example 17 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 570 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.30 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 16.1 ml/g and 8.8 ml/g, respectively. This adsorbent

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did not crack even in the immersion test using distilled water.

EXAMPLE 18

A 100 g portion of a powdery silica gel having a surface area of 840 m^2/g, an average pore diameter of 1.3 nm, and a pore volume of 0.37 ml/g was weighed out, and a 0.15 g portion of zirconium oxynitrate dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$) was weighed out.

Subsequently, the whole weighed zirconium oxynitrate dihydrate and the whole weighed powdery silica gel were dry-kneaded with an automatic mortar for 10 minutes. The mixed powder thus obtained was pelletized into cylindrical pellets having a diameter of 2.0 mm and a height of 3.0 mm. These moldings were heated with an electric furnace to 680°C at a heating rate of 2 °C/min in air and heat-treated at the temperature of 680°C for 3 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 3000:1 was obtained as a sample adsorbent of Example 18.

The sample adsorbent of Example 18 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 460 m^2/g, an average pore diameter of 1.2 nm, and a pore

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volume of 0.20 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 8.8 ml/g and 9.5 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

EXAMPLE 19

A 100 g portion of molded silica gel spheres having a surface area of 580 m^2/g, an average pore diameter of 1.3 nm, a pore volume of 0.30 ml/g, and a particle diameter of from 6 to 8 meshes was weighed out, and a 0.99 g portion of aluminum lactate ($Al[CH_3CH(OH)COO]_3$) was weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 550°C at a heating rate of 2 °C/min and heated at the temperature of 550°C in air for 3 hours.

The whole weighed aluminum lactate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 350°C in air at a heating rate of 2 °C/min, and heat-treated at the temperature of 350°C for 5 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 500:1 was obtained as a sample adsorbent of Example 19.

The sample adsorbent of Example 19 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 520 m^2/g, an average pore diameter of 1.3 nm, and a pore volume of 0.27 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 9.9 ml/g and 8.4 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

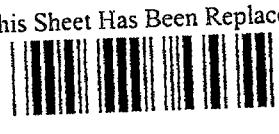
EXAMPLE 20

A 100 g portion of molded silica gel spheres having a surface area of 560 m^2/g, an average pore diameter of 3.6 nm, a pore volume of 0.65 ml/g, and a particle diameter of from 6 to 8 meshes was weighed out, and a 0.33 g portion of 40% aqueous titanium sulfate solution ($Ti(SO_4)_2aq$) was weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 600°C at a heating rate of 2 °C/min and heated at the temperature of 600°C in air for 5 hours.

The heat-treated molded silica gel was then immersed in the whole weighed 40% aqueous titanium

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sulfate solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 500°C in a nitrogen atmosphere at a heating rate of 2 °C/min, and heat-treated at the temperature of 500°C for 5 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 3000:1 was obtained as a sample adsorbent of Example 20.

The sample adsorbent of Example 20 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 500 m^2/g, an average pore diameter of 3.4 nm, and a pore volume of 0.54 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 8.7 ml/g and 8.4 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

COMPARATIVE EXAMPLE 11

As a sample adsorbent of Comparative Example 11, the same molded silica gel as that used in Example 12 was examined, without any treatment, for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 710 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.37 ml/g. It

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had a saturation water adsorption and a reversible isopentane adsorption of 64.1 ml/g and 8.9 ml/g, respectively. This adsorbent was immersed in distilled water. As a result, it cracked and powdered.

COMPARATIVE EXAMPLE 12

A 100 g portion of the same molded silica gel as in Example 12 and a 0.12 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) were weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 750°C at a heating rate of 2 °C/min and heated at the temperature of 750°C in air for 5 hours.

The whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 500°C under vacuum at a heating rate of 2 °C/min, and heat-treated at the temperature of 500°C for 3 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 5000:1 was obtained as a sample adsorbent of Comparative Example 12.

The sample adsorbent of Comparative Example 12 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 290 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.15 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 3.9 ml/g and 3.5 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

COMPARATIVE EXAMPLE 13

A 100 g portion of molded silica gel spheres having a surface area of 580 m^2/g, an average pore diameter of 1.5 nm, a pore volume of 0.30 ml/g, and a particle diameter of from 6 to 8 meshes was weighed out, and a 0.62 g portion of aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) was weighed out.

Subsequently, the molded silica gel was heated with a muffle furnace from room temperature to 450°C at a heating rate of 2 °C/min and heated at the temperature of 450°C in air for 5 hours.

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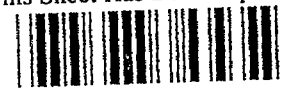


The whole weighed aluminum nitrate nonahydrate was dissolved in 100 ml of distilled water to prepare an aqueous solution. Thereafter, the heat-treated molded silica gel was immersed in the thus-prepared aqueous solution and allowed to stand for 15 hours. Subsequently, the impregnated molded silica gel was dried in an oven at 110°C for 15 hours, further heated with an electric furnace to 200°C in air at a heating rate of 2 °C/min, and heat-treated at the temperature of 200°C for 15 hours.

Through the above treatments, a silica gel based adsorbent having an atom number ratio of 1000:1 was obtained as a sample adsorbent of Comparative Example 13.

The sample adsorbent of Comparative Example 13 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 560 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.29 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 28.8 ml/g and 8.4 ml/g, respectively. This adsorbent was immersed in distilled water. As a result, it cracked and powdered.

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COMPARATIVE EXAMPLE 14

A sample adsorbent of Comparative Example 14 was obtained in the same manner as in Example 16, except that the atom number ratio was 100:1 and the temperature for the heat treatment after the molding into cylindrical pellets was 680°C.

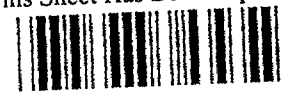
The sample adsorbent of Comparative Example 14 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 330 m^2/g, an average pore diameter of 1.5 nm, and a pore volume of 0.22 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 3.3 ml/g and 5.1 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

COMPARATIVE EXAMPLE 15

A 100 g portion of a powdery silica gel having a surface area of 430 m^2/g, an average pore diameter of 5.6 nm, and a pore volume of 0.80 ml/g was weighed out, and a 0.44 g portion of zirconium oxynitrate dihydrate ($ZrO(NO_3)_2 \cdot 2H_2O$) was weighed out.

Subsequently, the whole weighed zirconium oxynitrate dihydrate and the whole weighed powdery silica gel were dry-kneaded with an automatic mortar for

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10 minutes. The mixed powder thus obtained was pelletized into cylindrical pellets having a diameter of 2.0 mm and a height of 3.0 mm. These moldings were heated with an electric furnace to 500°C at a heating rate of 2 °C/min and heat-treated at the temperature of 500°C in air for 5 hours.

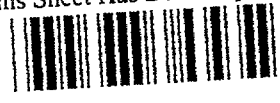
Through the above treatments, a silica gel based adsorbent having an atom number ratio of 1000:1 was obtained as a sample adsorbent of Comparative Example 15.

The sample adsorbent of Comparative Example 15 obtained was examined for adsorbent properties. As a result, the sample adsorbent was found to have a surface area of 340 m^2/g, an average pore diameter of 5.2 nm, and a pore volume of 0.65 ml/g. It had a saturation water adsorption and a reversible isopentane adsorption of 17.4 ml/g and 4.7 ml/g, respectively. This adsorbent did not crack even in the immersion test using distilled water.

(Discussion of Examples 12 to 20)

The adsorbents of Examples 12 to 20, which each contains one of the metals specified in the present invention in an atom number ratio within the specified range and has the adsorbent properties specified in the present invention, have a reversible isopentane

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adsorption of 7.7 mg/l or larger and a saturation water vapor adsorption of 17.8 mg/l or smaller. They are superior to conventionally known adsorbents in both hydrophobicity and VOC-adsorbing ability.

The adsorbents of Examples 14 to 18 and 20, in which the heat treatment temperature was 500°C or higher, have a reversible isopentane adsorption of 7.7 mg/l or larger and a saturation water adsorption of 16.1 mg/l or smaller irrespective of the Si/M ratio. In particular, the adsorbents of Examples 16 and 18, in which the heat treatment temperature was 550°C or higher, have a larger reversible isopentane adsorption and a smaller saturation water adsorption.

Furthermore, the adsorbents of Examples 13, 16, and 19, in which the Si/M ratio is 500, have a reversible isopentane adsorption of 8.4 mg/l or larger and a saturation water vapor adsorption of 12.2 mg/l or smaller irrespective of the heating temperature.

The adsorbent of Example 12 has the largest saturation water adsorption among those of the Examples because the heating temperature was low and the Si/M ratio is 1000. On the other hand, the adsorbent of Example 13, which differs from Example 12 only in Si/M ratio, has a far smaller saturation water vapor

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adsorption than that of Example 12 because the Si/M ratio therein is 500.

(Discussion of Comparative Examples 11 to 15)

As apparent from Comparative Example 11, the adsorbents not containing any of the metals specified in the present invention have a considerably large saturation water adsorption, readily crack, and have poor water resistance. These adsorbents are practically unusable.

The adsorbents which do not have the adsorbent properties specified in the present invention, as in Comparative Examples 12, 14, and 15, have a far smaller reversible isopentane adsorption than the adsorbents of the Examples although almost equal in saturation water adsorption to the adsorbents of the Examples. It is therefore difficult to put these adsorbents to practical use. In particular, the adsorbent of Comparative Example 5 has adsorbent properties outside the ranges specified in the present invention because the raw silica gel had a considerably small specific surface area and a large average pore diameter, although it contains one of the metals specified in the present invention in an Si/M ratio within the specified range and has undergone the heat treatment specified in the

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present invention. As a result, the adsorbent of Comparative Example 5 has a large saturation water adsorption.

Furthermore, the adsorbents having a metal content outside the range specified in the present invention have a considerably reduced specific surface area and a reduced reversible isopentane adsorption, as shown in Comparative Example 14. These adsorbents are hence unsuitable for VOCs.

The adsorbents which have not undergone the heat treatment specified in the present invention have a far larger saturation water adsorption than the adsorbents of the Examples, readily crack, and have poor water resistance, although almost equal in reversible isopentane adsorption to the adsorbents of the Examples, as shown in Comparative Example 13. It is therefore difficult to put these adsorbents to practical use. In general, lower heating temperatures result in larger water vapor adsorptions, susceptibility to cracking, and poor water resistance. Furthermore, such adsorbents have a reduced isopentane adsorption because water vapor is adsorbed thereonto in a large amount, and are hence unsuitable for VOCs. The adsorbent of Comparative Example 13 has a larger water vapor adsorption than the adsorbents of Examples 12 to 20 and poor water

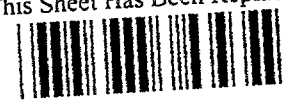
resistance because of the too low heating temperature, although improved in water resistance as compared with the adsorbent of Comparative Example 11 because it contains one of the metals specified in the present invention in an Si/M ratio within the specified range. The adsorbent of Comparative Example 13 is hence unsuitable for VOCs.

Conversely, too high heating temperatures for the pretreatment are undesirable in that the results are a considerably reduced surface area and a reduced reversible isopentane adsorption, as can be seen from Comparative Example 12. Furthermore, although the adsorbent of Comparative Example 12 contains one of the metals specified in the present invention, the metal addition has produced almost no effect because the Si/M ratio therein is larger than the Si/M ratios specified in the present invention, i.e., the content thereof is too low.

(Comparative Discussion of Examples 12 to 20 and Comparative Examples 11 to 15)

As can be seen from a comparison between Examples 12 to 20 and Comparative Examples 11 to 15, the adsorbents of the present invention are equal or superior in VOC-adsorbing ability to the adsorbents of

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the Comparative Examples. On the other hand, they are superior in hydrophobicity.

Evaluation with respect to VOC Selectivity

Sample adsorbents were examined for VOC selectivity as a factor indicating VOC-adsorbing ability. The VOC selectivities of the sample adsorbents of Examples 12 to 20 and Comparative Examples 11 to 15 were determined by the above-described method with respect to the specified VOCs as shown in Table 8. The results shown in Table 8 were obtained.

As Table 8 shows, the sample adsorbents of Examples 12 to 20 each has a VOC selectivity of 80% or higher, which is far higher than the VOC selectivities of 73% or lower for the sample adsorbents of Comparative Examples 11 to 14.

Comparisons between the sample adsorbents of Example 13 and Comparative Example 13, between the sample adsorbents of Example 14 and Comparative Example 11, between the sample adsorbents of Example 15 and Comparative Example 12, between the sample adsorbents of Example 15 and Comparative Example 14, and between the sample adsorbents of Example 17 and Comparative Example 15, wherein each Example uses the same VOC adsorbate as the Comparative Example compared therewith, show that

the sample adsorbent of each of all these Examples, where different VOCs are used, has a VOC selectivity higher by about from 17% to 55% than that of the sample adsorbent of the compared Comparative Example. In particular, the VOC selectivity of the sample adsorbent of Example 14 is higher by more than 55% than that of the sample adsorbent of Comparative Example 11, when isopentane is used.

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Table 8

	Name of adsorbate VOC	VOC adsorption (ml/g (stp))	VOC selectivity (%)
Example 12	formic acid	71.5	80.1
Example 13	pyridine	50.7	80.6
Example 14	isopentane	50.4	85.7
Example 15	MEK	62.4	92.9
Example 16	formic acid	45.0	81.1
Example 17	methyl acrylate	65.1	80.2
Example 18	dichloromethane	57.2	86.7
Example 19	trichloromono-fluoromethane	46.0	82.3
Example 20	MEK	59.4	87.2
Comp. Ex. 11	isopentane	26.3	29.1
Comp. Ex. 12	dichloromethane	8.9	69.5
Comp. Ex. 13	pyridine	25.8	47.3
Comp. Ex. 14	MEK	9.1	73.4
Comp. Ex. 15	methyl acrylate	19.7	53.1

It can be seen from the above that the sample adsorbents of the Examples have an exceedingly high VOC-adsorbing ability.

EXAMPLE 21

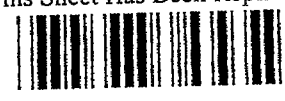
A gas containing toluene in a concentration of 1000 ppm was treated in Fig. 1 at a flow rate of from 10 to 25 l/min. The operation conditions are as follows and sequence control was used for the whole operation.

(Operation Conditions)

- Switching interval between adsorption step and desorption step: 5 minutes
- Mode: PSA process comprising adsorption at ordinary pressure and desorption at reduced pressure
- Adsorbent: hydrophobized silica gel
- Purge amount: air, 13 l/min
- Degree of vacuum in desorption: 60 mmHg
- Cooler: cooling with water; temperature, 10°C

The results are as follows. The feed gas, which initially had a toluene concentration of 1000 ppm, was wholly returned to the inlet of the adsorption column, without leaving even a drop of condensate in the reservoir 5. This circulation was repeated. As a result, at 240 minutes after initiation of the operation, the toluene concentration in the desorbed gas reached 15000 ppm and a condensate began to accumulate in the reservoir 5. The resultant treated gas was discharged as moist air containing toluene vapor in an amount not larger than 40 ppm into the atmosphere from the top of the adsorption column 2a (the adsorption column 2b after switching to a desorption step) omitted in Fig. 1.

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INDUSTRIAL APPLICABILITY

As described above, the adsorbents according to the present invention are useful in techniques for recovering VOCs emitted into the air from small-scale general VOC emission sources, such as gas stations, fuel oil shipping facilities, oil tank stations, the cleaning industry, the coating industry, and the like. When used in combination with cooling condensation, the adsorbents are effective in practical recovery with simple equipment without necessitating facilities such as a chilling unit.



CLAIMS

1. An adsorbent which comprises a porous molded material comprising silica as the main component and having a specific surface area of from 400 to 700 m^2/g, an average pore diameter of from 0.4 to 3.0 nm, and a water vapor adsorption of from 3 to 10 ml-water-vapor/g-adsorbent, and selectively adsorbs gases of volatile organic compounds having 1 to 12 carbon atoms.

2. A process for preparing an adsorbent which selectively adsorbs gases of volatile organic compounds having 1 to 12 carbon atoms, comprising:

heating molded pellets of either silica or a silica gel which have a specific surface area of 600 m^2/g or larger, a pore volume of from 0.05 to 0.5 cm^3/g, and an average pore diameter of from 0.4 to 3.0 nm to a predetermined temperature of from 550°C to 700°C at a heating rate of from 1 to 20 °C/min, and keeping the pellets at the predetermined temperature for a predetermined period of time.

3. An adsorbent produced by the adsorbent production process of claim 2, which has a decrease ratio in specific surface area of 40% or less, and has a

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water vapor adsorption of from 3 to 10 ml-water-vapor/g-adsorbent.

4. An adsorbent which comprises a porous molded silica gel having been obtained by adding at least one organic compound selected from the group consisting of carboxylic acids and derivatives thereof, aldehydes and derivatives thereof, and thermally decomposable high-molecular organic compounds to a raw silica gel in an amount of from 1 to 30% by weight based on the adsorbent and then heat-treating the mixture at a temperature of from 400 to 750°C and having a specific surface area of from 450 to 700 m^2/g and an average pore diameter of from 1.7 to 5.5 nm, and selectively adsorbs volatile organic compounds having 1 to 12 carbon atoms.

5. A process for preparing an adsorbent comprising silica as the main component and selectively adsorbing volatile organic compounds having 1 to 12 carbon atoms, comprising:

an addition step in which at least one organic compound selected from the group consisting of carboxylic acids and derivatives thereof, aldehydes and derivatives thereof, and thermally decomposable high-molecular organic compounds is added to a raw silica gel

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in an amount of from 1 to 30% by weight based on the adsorbent, and

a heat treatment step in which the silica gel to which the compound has been added is kept at a temperature in the range of from 400 to 750°C for a predetermined period of time.

6. The process for preparing an adsorbent of claim 5, which comprises, prior to the heat treatment step, a molding step in which the silica gel after the addition step is molded to obtain a molded silica gel.

7. The process for preparing an adsorbent of claim 5 or 6, wherein, in the heat treatment step, the silica gel to which the compound has been added is heated to the predetermined temperature at an average heating rate of from 0.5 to 20 °C/min.

8. An adsorbent which comprises a molded silica gel which has been obtained by incorporating at least one metal selected from aluminum, zirconium, and titanium into a silica gel in such an amount that the ratio of the number of metal atoms in the silica gel to the number of silicon and metal atoms therein is from 200:1 to 4000:1 and then heat-treating the resultant

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mixture at a temperature in the range of from 300 to 700°C and having a specific surface area of from 400 to 600 m^2/g and an average pore diameter of from 1.0 to 4.0 nm, and selectively adsorbs volatile organic compounds having 1 to 12 carbon atoms.

9. A process for preparing an adsorbent selectively adsorbing volatile organic compounds having 1 to 12 carbon atoms, comprising:

a deposition step in which either at least one metal selected from aluminum, zirconium, and titanium or a compound of the metal is deposited on a molded or powdery silica gel having a specific surface area of 550 m^2/g or larger and an average pore diameter of from 1.0 to 4.0 nm in such an amount that the ratio of the number of metal atoms in the silica gel to the number of silicon and metal atoms therein is from 200:1 to 4000:1 and

a heat treatment step in which the molded silica gel after the deposition step is heat-treated at 300°C to 700°C.

10. The process for preparing an adsorbent of claim 9, which comprises, prior to the heat treatment

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step, a step in which the powdery silica gel after the deposition step is molded to form a molded silica gel.

11. The process for preparing an adsorbent of claim 9 or 10, which comprises, prior to the deposition step, a pretreatment step in which the molded silica gel is preliminarily heat-treated at a temperature of from 500 to 700°C.

12. The adsorbent of any one of claims 1, 3, 4, and 8, which has a VOC selectivity as defined by the following equation of 80% or more:

VOC selectivity = $\{(A)/(A + B)\} \times 100$

wherein A is the equilibrium adsorption (ml/g (stp)) of a volatile organic compound on the adsorbent at a temperature of 20°C and a pressure which is one-tenth the saturation vapor pressure of the volatile organic compound at a temperature of 20°C, and

B is the equilibrium adsorption (ml/g (stp)) of water vapor on the adsorbent at a pressure of 2 mmHg and a temperature of 20°C.