

Title of the Invention:

Volatile Organic Compound Adsorbent and Resin
Composition blended with the Volatile Organic Compound
Adsorbent

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Technical Field:

[0001]

This invention relates to a volatile organic compound
adsorbent comprising an MFI type zeolite.

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Background Art:

[0002]

Zeolite is a crystalline aluminosilicate having SiO_2 ,
 Al_2O_3 and the like in the zeolite framework and, further, having
15 regular channels (pores). Specifically, the MFI type zeolite
is rich in silica, and has been widely known to contain pores
of a 10-membered ring structure ($5.1 \times 5.5 \text{ \AA}$ and/or $5.3 \times 5.6 \text{ \AA}$).

[0003]

20 It has been known that Al_2O_3 in the zeolite framework
affects the hydrophilic property, that the larger the amount
of Al, the higher the hydrophilic property and that the smaller
the amount thereof, the lower the hydrophilic property. The
silica-rich MFI type zeolite contains Al in small amounts and
25 has a low hydrophilic property; i.e., it exhibits a high degree
of adsorbing property for the hydrophobic organic components.
Moreover, since the silica-rich MFI type zeolite has a pore size
close to the size of a low-molecular hydrocarbon, there has been
proposed to use it as an adsorbent for adsorbing organic
30 compounds (see patent documents 1 to 3).

[0004]

Moreover, the MFI type zeolite has an action for reducing
odor specific to the degenerating resins (hereinafter resin
odor) (see a patent document 4).

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[0005]

Here, it has been known that volatile organic compounds (hereinafter often abbreviated as VOCs) such as toluene, xylene, ethyl acetate and the like, greatly affect the environment and become a cause of, for example, photochemical smog. Therefore, the Air Pollution Control Law strictly controls the concentration of VOCs emitted and scattered from the fixed sources of generation, such as factories. Therefore, it has been urged to provide an adsorbent that is capable of efficiently removing the volatile organic compounds from the emitted gases.

[0006]

The above-mentioned MFI type zeolite is highly capable of adsorbing a variety of organic compounds and has, therefore, been frequently used as a VOC adsorbent. However, since its capacity of adsorption is small, the MFI type zeolite had to be used in large amounts to attain the desired effect. Therefore, it has been desired to improve the capability and capacity of the MFI type zeolite for adsorbing VOCs. Specifically, it has been desired to provide an adsorbent that is capable of adsorbing VOCs such as toluene and the like to a sufficient degree even when they are present in the atmosphere at low concentrations.

Prior Art Documents:

Patent Documents:

[0007]

Patent document 1: JP-H01-171554

Patent document 2: JP-H09-253483

Patent document 3: JP-A-2003-126689

Patent document 4: JP-A-2002-069315

Outline of the Invention:

Problems that the Invention is to Solve:

[0008]

It is, therefore, an object of the present invention to

provide a volatile organic compound adsorbent that exhibits excellent adsorbing capability even when the volatile organic compounds are present at low concentrations.

Another object of the present invention is to provide an
5 adsorbent that exhibits excellent adsorbing capability for, specifically, toluene.

[0009]

A further object of the present invention is to provide
a resin composition blended with the volatile organic compound
10 adsorbent.

Means for Solving the Problems:

[0010]

The present inventors have conducted a lot of experiments
15 concerning the capabilities of zeolites for adsorbing volatile organic compounds. As a result, the inventors have discovered the fact that the MFI type zeolite obtained by the synthesis at a low temperature exhibits excellent capability for adsorbing the VOC (toluene) that is present at a low
20 concentration in the atmosphere, and have thus completed the present invention.

[0011]

According to the present invention, there is provided a volatile organic compound adsorbent including an MFI type
25 zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratio) of not less than 50, the zeolite having a spacing (d-value) on a plane (053) of not more than 2.99 Å in an X-ray diffraction spectrum and a nitrogen-adsorbing capability of not less than 100 (cm^3/g) under a nitrogen partial pressure P_{N_2} (P/P_0) of 0.005.

30 [0012]

With the volatile organic compound adsorbent of the present invention, it is desired that:

- (1) The $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratio) is not less than 90;
- (2) A toluene-adsorbing capability is not less than 8.2% by
35 mass under a toluene partial pressure P_T (P/P_0) of 0.01; and

(3) The content of an alkali metal calculated as an oxide thereof is suppressed to be not more than 0.1% by mass.

[0013]

According to the present invention, further, there is provided a resin composition obtained by blending a resin with the above-mentioned volatile organic compound adsorbent.

[0014]

With the resin composition obtained by blending the resin with the adsorbent of the present invention, it is desired that:

- 10 (1) The adsorbent is contained in an amount of 0.005 to 100 parts by mass per 100 parts by mass of the resin; and
(2) The resin is a thermoplastic resin.

Effects of the Invention:

15 [0015]

The volatile organic compound adsorbent of the present invention, as demonstrated in Examples appearing later, has a toluene-adsorbing capability of not less than 8.2% by mass and, in the largest case, not less than 9.0% by mass in an atmosphere of a toluene partial pressure P_T (P/P_0) of 0.01, i.e., in an atmosphere containing toluene in very small amounts. None of the conventional MFI type zeolite adsorbents show the toluene adsorbing capability of not less than 8.2% by mass in the atmosphere of such a low toluene concentration. Therefore, the volatile organic compound adsorbent of the present invention can be favorably used in the facilities for purifying the environment, such as in the chemical plants in a manner of, for example, being carried by an exhaust rotor that has a honeycomb structure.

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Brief Description of the Drawings:

[0016]

[Fig. 1] It is a diagram of an X-ray diffraction image of a volatile organic compound adsorbent comprising an MFI type zeolite obtained in Example 2.

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[Fig. 2] It is a diagram of an X-ray diffraction images of planes (053) of Example 3 and Comparative Examples 2 and 3.

[Fig. 3] It is a diagram of isothermal lines of nitrogen adsorption measured in Example 2 and Comparative Examples 1, 2 and 3.

[Fig. 4] It is a diagram of isothermal lines of toluene adsorption measured in Example 2 and Comparative Examples 2 and 3.

[Fig. 5] It is a scanning type electron microphotograph of a volatile organic compound adsorbent comprising an MFI type zeolite obtained in Example 1.

[Fig. 6] It is a scanning type electron microphotograph of a volatile organic compound adsorbent comprising an MFI type zeolite obtained in Example 6.

Modes for Carrying Out the Invention:

[0017]

An adsorbent comprising an MFI type zeolite of the present invention is used for adsorbing or removing volatile organic compounds. The volatile organic compounds stand for organic compounds having boiling points in a range of 50 to 260°C under the atmospheric pressure. Examples thereof include toluene, xylene, ethyl acetate, ethanol, benzene, methyl ethyl ketone, dichloroethane, trichloroethane and the like and, specifically, toluene.

[0018]

<MFI type zeolite>

The MFI type zeolite is used as an adsorbent, and is forming pores in the form of a 10-membered ring which is specific to the zeolite and, therefore, exhibits X-ray diffraction peaks as shown in Fig. 1. For instance, it exhibits sharp diffraction peaks near $2\theta = 7.9^\circ$ due to the plane (011), near $2\theta = 8.9^\circ$ due to the plane (200) and near $2\theta = 23.1^\circ$ due to the plane (051).

The above zeolite is rich in silica, has an $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole

ratio) of not less than 50, preferably, not less than 90, more preferably, not less than 100 and, most preferably, not less than 5,000 and, therefore, has a low hydrophilic property, i.e., has excellent capability for adsorbing highly hydrophobic organic compounds. On the other hand, the zeolite that contains much aluminum (the above mole ratio of less than 50) has a high hydrophilic property and is not capable of excellently adsorbing the VOCs.

[0019]

10 The MFI type zeolite used in the present invention is produced by the reaction at a low temperature (80 to 130°C). As a result, the MFI type zeolite has a spacing (d-value) on the plane (053) of not more than 2.99 Å in an X-ray diffraction spectrum and a nitrogen-adsorbing capability of not less than 15 100 (cm³/g) and, preferably, not less than 103 (cm³/g) under a nitrogen partial pressure P_{N_2} (P/P_0) of 0.005. The reasons will be described later about why the above d-value and the nitrogen-adsorbing capability can be obtained by the reaction at the low temperature.

20 [0020]

 The above d-value represents a spacing between the specific planes possessed by the pores in the zeolite. The d-value that is small means that the zeolite is free of strain and in which the pores are homogeneously distributed and have large porous volumes.

 In connection with the above-mentioned small d-value, the MFI type zeolite contains the pores of the above-mentioned micro sizes that are distributed therein densely and homogeneously. As a result, the MFI type zeolite shows a large 30 nitrogen-adsorbing capability even in an atmosphere in which the nitrogen partial pressure P_{N_2} (P/P_0) is as low as 0.005 as described above. In other words, the above nitrogen-adsorbing capability means that the pores of the above micro sizes have been densely distributed in the MFI type zeolite which, 35 therefore, exhibits very excellent capability for adsorbing the

volatile organic compounds and, specifically, toluene.

[0021]

It is, further, desired that the MFI type zeolite contains an alkali metal (hereinafter alkali) in an amount, calculated as an oxide thereof, that is suppressed to be not more than 1.70% by mass, preferably, not more than 1.25% by mass and, specifically, not more than 0.1% by mass. That is, the alkali components (e.g., Na and K) are mixed as unavoidable impurities into the zeolite. If the amount thereof is large, however, the zeolite has increased hydrophilic property and greatly loses its capability for adsorbing the organic components. According to the present invention, however, the amount of such alkali components has been suppressed to be very small to effectively avoid a decrease in the capability for adsorbing the organic compounds. As a result, the MFI type zeolite secures a large capability for adsorbing the VOCs. For instance, as demonstrated in Examples appearing later, the MFI type zeolite used in the present invention has a toluene-adsorbing capability of not less than 8.2% by mass in an atmosphere of a toluene partial pressure P_T (P/P_0) of 0.01. The MFI type zeolite has the toluene-adsorbing capability of not less than 9% by weight and, specifically, close to 10% by mass if the amount of alkali therein is suppressed to be not more than 0.1% by mass calculated as an oxide thereof.

[0022]

<Production of the MFI type zeolite>

The above-mentioned MFI type zeolite is produced by reacting (crystalizing) a silica source and an alumina source by heating the silica source and the alumina source in a mixed gel that contains the silica source and the alumina source in the presence of template and seed crystals and, preferably, in the further presence of an alkali metal hydroxide for preparing the starting material that will be described later.

[0023]

The above silica source is desirably the highly pure SiO_2

from which impurities such as Na_2O and Al_2O_3 have been removed to some extent, such as tetraethylorthosilicate, colloidal silica, dry silica gel powder and silica hydrogel. These silica sources once dissolve in an aqueous solution during the reaction and are rebuilt into the MFI type zeolite. Here, if there are contained little impurities or unreactive components that are unnecessary for the reaction, then the crystallization of the MFI type zeolite is not much affected by the kind of the silica source.

From the aspect of cost, however, it is desired to use the dry silica gel powder or the silica hydrogel and, specifically, to use the silica hydrogel since the MFI type zeolite can be produced therefrom through a relatively simple method. The silica hydrogel can be easily obtained by gradually adding a silicic acid alkali such as sodium silicate dropwise to a mineral acid such as sulfuric acid, adjusting the final pH to be about 3.0 to about 9.0, effecting the filtration and effecting the washing until the pH of the washing water that is discharged acquires a pH of about 5.0 to about 7.0. The silica hydrogel can be produced by being heated while mixing the starting materials together or before or after the washing with water, or can be produced at normal temperature.

As the alumina source, there can be used, for example, aluminum sulfate, basic aluminum sulfate or sodium aluminate. It is, however, specifically desired to use the sodium aluminate.

When it is attempted to obtain an MFI type zeolite having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of, for example, 112 which is higher than the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of the desired MFI type zeolite, then the mixed gel contains the Si component and the Al component so as to have the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of, for example, 120. Usually, the mixed gel is obtained by mixing the silica source and the alumina source together in an aqueous medium at normal temperature.

[0024]

The silica source and the alumina source are so mixed together that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratio) becomes a predetermined quantity ratio. When it is attempted to produce the MFI type zeolite containing specifically much Si component (e.g., mole ratio of not less than 1000), however, the alumina source may not be used. This is because, the starting materials used for the industrial purposes often contain Al components in small amounts as unavoidable impurities.

[0025]

10 The mixed gel containing the silica source and the alumina source may, further, contain a template, seed crystals and, preferably, an alkali metal hydroxide. The mixed gel containing the seed crystals is crystallized by the reaction at a low temperature in the presence of the template and the seed crystals to thereby obtain the MFI type zeolite.

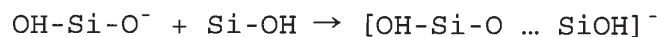
15 There is no specific limitation on the method of adding the template, the seed crystals or the alkali metal hydroxide. They can be mixed in advance to part or whole of the mixed gel and/or to part or whole of the starting materials of the mixed gel, prior to the crystallization.

[0026]

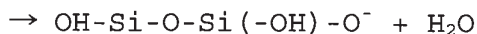
The template is a structure-directing agent for forming pores of the 10-membered ring form specific to the MFI type zeolite, and is an amine compound having an n-alkyl group with 2 to 4 carbon atoms and a nitrogen cation in the molecules thereof. Examples thereof are a salt of a cation and an anion (e.g., Br^-) of a tetraalkyl (ethyl, n-propyl or n-butyl) ammonium, and a hydroxide of the above ammonium.

[0027]

30 That is, in the reaction of the silica-alumina hydrosol (SiO chain by condensation), an intermediate product having a negative electric charge is formed to form a chain of Si-O-Si as expressed by the following schematic formula,



35 $\rightarrow \text{OH-Si-O-Si}^--\text{OH}$



In forming the above Si-O-Si chain, the cation of the template protects the intermediate product and, at the same time, the Si-O-Si chain is formed so as to surround the cation of the template. As a result, there is formed the 10-membered ring structure specific to the MFI type zeolite.

[0028]

The template, if it is, for example, a tetrapropylammonium bromide (TPA-Br), is used in an amount of TPA/SiO₂ = 0.03 to 0.20 (mole ratio) with respect to the Si component in the mixed gel. The amount, however, greatly differs depending on the kind of the template and, specifically, on the number of carbon atoms in the alkyl group.

Though not needed when the hydroxide of the above quaternary ammonium is used as the template, an alkali metal hydroxide (e.g., caustic soda, etc.) is added when a salt of the quaternary ammonium and an anion such as Br or Cl is used as the template, the alkali metal hydroxide being added in an amount of A₂O/SiO₂ = 0.01 to 0.20 (mole ratio, A is an alkali metal element) with respect to the Si component in the mixed gel in order to dissolve the silica source. In this case, the larger the amount of the alkali metal hydroxide that is added, the shorter the time required for the crystallization. If the A₂O/SiO₂ ratio exceeds 0.20, however, the hydrophilically working alkali metal remains in large amounts in the MFI zeolite that is obtained, and the adsorbing capability of the present invention may not be often exhibited to a sufficient degree. Therefore, the A₂O/SiO₂ ratio is, preferably, not more than 0.15 and, particularly preferably, not more than 0.10.

[0029]

To produce the above-mentioned MFI type zeolite, the reaction must be carried out at a low temperature or, concretely at 80 to 130°C, preferably, at 95 to 120°C and, particularly preferably at 95 to 98°C. Therefore, the above reaction must be carried out in the presence of seed crystals. This promotes

the crystallization which, therefore, can be completed in a short period of time, for example, in not longer than 48 hours and, specifically, in not longer than 20 hours yet carrying out the reaction at a low temperature.

5 As the seed crystals, it is necessary to use the MFI type zeolite that was prepared in advance. Among those produced by the methods that will be described later, however, it is also allowable to use an MFI type zeolite that contains the template or an MFI type zeolite from which the template has been removed
10 by, for example, firing. The seed crystals are suitably pulverized and are added in an amount of 0.02 to 20 parts by mass and, preferably, 0.05 to 5.0 parts by mass per 100 parts by mass of the SiO_2 which is the Si component in the mixed gel.

 If the amount of the seed crystals is not more than 0.05
15 parts by mass, the effect is weak for shortening the time for crystallization. If the amount of addition is too large, the composition of the seed crystals affects the composition of the obtained MFI type zeolite. Besides, formation of the cores and shells also cause the formation of undesired interface which
20 hinders the formation of the densely distributed pores and which, therefore, is not desirable. Specifically, despite the amount of addition is not less than 5.0 parts by mass, there is no appreciable change in the time required for the crystallization; i.e., the seed crystals are merely used in
25 increased amounts driving up the cost, which is not desirable, either.

[0030]

 Further, as described above, the mixed gel (mixed gel containing the seed crystals) is reacted at 80 to 130°C in the
30 presence of the template and the seed crystals, and there is obtained a silica-rich MFI type zeolite having the above-mentioned d-value and the nitrogen-adsorbing capability.

 When the MFI type zeolite is produced by a conventional
35 method, for example, the reaction temperature is set to be as

high as about 180°C or about 150°C at the lowest, enabling the crystallization to be completed in short periods of time. According to the study conducted by the present inventors, however, if the reaction is carried out at temperatures of not
5 lower than 130°C, the obtained MFI type zeolite acquires a d-value (spacing between the planes (053)) which is in excess of 2.99 Å and has a nitrogen-adsorbing capability which is smaller than 100 (cm³/g) under a nitrogen partial pressure P_{N_2} (P/P_0) of 0.005. Though the reason has not been fully clarified
10 yet, the inventors presume that if the reaction is carried out at a high temperature, the template is thermally decomposed while the MFI type zeolite is being crystallized or, even if the template is not thermally decomposed, vibration of the template is amplified by the heat energy thereof and, as a result,
15 the template exhibits decreased effect for protecting the intermediate. Presumably, therefore, the crystal structure of the obtained MFI type zeolite is distorted or the pores that are formed are distorted.

Namely, since the present invention carries out the
20 reaction at the low temperature as described above, the template is prevented from being decomposed or vibrated by the heat energy. As a result, the obtained zeolite is prevented from being distorted or the pores therein are prevented from deformed permitting, therefore, the pores of a uniform size to be densely
25 distributed. It is, therefore, considered that the obtained MFI type zeolite has a small d-value of spacing between the specific planes (053) and exhibits a large nitrogen-adsorbing capability. Specifically, the d-value of the plane (053) that is as small as not more than 2.99 Å like in the present invention
30 means that the MFI type zeolite has a very dense crystal structure in which the pores of micro sizes are distributed densely and homogeneously. Usually, the d-value of the zeolite can be analyzed involving little confusion with other peaks in the range of XRD measurement, and it is desired to use a peak
35 on the side of a relatively high angle (e.g., near 30°). In

the case of the MFI type zeolite, the plane (053) meets this condition, from which it is analyzed that a volatile organic compound adsorbent comprising the MFI type zeolite of the present invention has a dense crystal structure.

5 The MFI type zeolite can be crystallized even if the reaction temperature is not higher than 80°C. In this case, however, the reaction proceeds very slowly and becomes impracticable.

[0031]

10 According to the present invention as described above, the zeolite that is obtained is free of distortion and contains the pores of a uniform size that are densely distributed therein without being deformed. Therefore, the zeolite has a high BET specific surface area as will be demonstrated in Examples
15 appearing later. That is, the volatile organic compound adsorbent of the present invention has a BET specific surface area of not less than 430 m²/g, preferably, not less than 440 m²/g and, specifically preferably, not less than 450 m²/g.

[0032]

20 So far as the reaction temperature lies in the above-mentioned low-temperature region, furthermore, the reaction may be carried out under the atmospheric pressure or may be carried out under an elevated pressure by using an autoclave or the like. Even if carried out under the elevated
25 pressure, however, the reaction does not bring about any advantage. That is, the crystallization is promoted to a sufficient degree even if the reaction is carried out under the atmospheric pressure while using the seed crystals. From the viewpoint of cost, therefore, it is desired to carry out the
30 reaction under the atmospheric pressure.

[0033]

After the reaction, the zeolite is filtered, washed with water and dried in a customary manner and is, thereafter, fired at a temperature of about 500 to about 800°C for about 0.5 to
35 about 10 hours. There is thus obtained the desired MFI type

zeolite from which the template has been removed and containing the pores that are densely distributed therein, the MFI type zeolite being suited for adsorbing VOCs and, specifically, toluene.

5 [0034]

If alkali components such as Na and K are much used in the synthesis of the zeolite, then the alkali content becomes large. The alkali components work to impart hydrophilic property and, therefore, the obtained MFI type zeolite exhibits greatly decreased capability for adsorbing organic compounds. In such a case, it is desired that the MFI type zeolite obtained through the step of firing is dispersed again in an aqueous solution and from which the alkali components are removed by a dealkalization method by using an acid such as hydrochloric acid or sulfuric acid or by a series of dealkalization methods consisting of an ion exchange of alkali and ammonium by using various kinds of ammonium salts and a subsequent step of firing for removing ammonium.

Specifically, it is desired to employ the series of dealkalization methods by using various kinds of ammonium salts. In this case, it is desired to use the ammonium chloride in an amount of about 10 to about 200 parts by mass with respect to, for example, the MFI type zeolite after it has been fired. The subsequent firing for removing the ammonium is carried out, desirably, at 300 to 600°C for about 0.5 to about 10 hours.

25 [0035]

The thus obtained MFI type zeolite, usually, has a median diameter of 0.1 to 20 μm and, preferably, 0.5 to 10 μm , and is, preferably, used being suitably pulverized into a powdery form. By taking the easiness of handling into consideration, further, the MFI type zeolite is used with its grain size being adjusted into 1.0 to 4.0 μm . When used being kneaded with, for example, a resin composition or being mixed into a liquid that contains a hydrophobic solvent such as paint or coating agent, however, the MFI type zeolite may be used being more

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finely pulverized into the order of sub-microns (median diameter of 0.1 to 1.0 μm) to improve the dispersion property or to increase the specific surface area. When charged into a facility such as adsorption column or adsorption tower, furthermore, the MFI type zeolite is suitably mixed, for example, with a binder that is usually used and is molded into granules. [0036]

The volatile organic compound adsorbent comprising the above-mentioned silica-rich MFI type zeolite of the present invention is highly capable of adsorbing volatile organic compounds such as toluene, xylene and ethyl acetate, and is capable of effectively adsorbing and removing these compounds even from the atmosphere in which these compounds are present at low concentrations. Therefore, the adsorbent can be suitably used in a facility for purifying environment by, for example, being carried by an exhaust rotor that has a honeycomb structure in chemical plants or factories that emit gases containing volatile organic compounds.

[0037]

The volatile organic compound adsorbent of the present invention having the above-mentioned features is added to a resin to prepare a resin composition and from which a master batch is, preferably, prepared to form a variety of articles such as films and various materials. In this case, the volatile organic compound adsorbent of the invention may be added alone to the resin or may be added thereto in combination with other adsorbents or additives. There is no limitation on the amount of the volatile organic compound adsorbent of the invention that is added. The adsorbent, however, is added, for example, in an amount in a range of 0.001 to 1000 parts by mass and, preferably, 0.005 to 100 parts by mass per 100 parts by mass of the resin. However, when the adsorbent of the present invention is added to the resin to adsorb the odor specific to the resin that is generating from the unreacted monomer or the degenerating monomer at the time of processing the resin, it

is desired that the adsorbent is used in an amount of 0.005 to 10 parts by mass per 100 parts by mass of the resin.

Further, by adding the volatile organic compound adsorbent of the invention to the resins that are used as automotive members and building materials, the effect can be expected for improving living environment, such as adsorbing odors specific to new cars and new buildings and, specifically, adsorbing substances (toluene and aldehydes) that are the causes of sick building syndromes. By having the fibers contain the adsorbent of the present invention in the step of treating the fibers, furthermore, it is allowed to produce high-function fibers having deodorizing function. In this case, the adsorbent is contained in an amount of, desirably, 1 to 100 parts by mass per 100 parts by mass of the fiber.

[0038]

As the base resin, there can be used either a thermoplastic resin or a thermosetting resin. From the standpoint of formability, however, the thermoplastic resin is preferred. Described below are examples of the thermoplastic resin.

Olefin resins such as low-density polyethylene, high-density polyethylene, polypropylene, poly 1-butene, poly 4-methyl-1-pentene, or random or block copolymers of α -olefins like ethylene, propylene, 1-butene or 4-methyl-1-pentene, or cyclic olefin copolymers thereof;

Ethylene-vinyl type copolymers such as ethylene-vinyl acetate copolymer, ethylene-vinyl alcohol copolymer and ethylene-vinyl chloride copolymer;

Styrene type resins such as polystyrene, acrylonitrile-styrene copolymer, ABS and α -methylstyrene-styrene copolymer;

Vinyl type resins such as polyvinyl chloride, polyvinylidene chloride, vinyl chloride-vinylidene chloride copolymer, methyl polyacrylate and methyl polymethacrylate;

Polyamide resins such as nylon 6, nylon 6-6, nylon 6-10, nylon 11 and nylon 12;

Polyester resins such as polyethylene terephthalate (PET), polybutylene terephthalate, polyethylene naphthalate and copolymerized polyesters thereof;

Polycarbonate resins;

5 Polyphenylene oxide resins; and

Biodegradable resins such as polylactic acid.

The above-mentioned thermoplastic resins can be used each in a single kind but can also be used as a blend of two or more kinds thereof.

10 In the present invention, specifically, the olefin type resin and the polyester resin are preferred, and the olefin type resin is most desired as the base resin.

[0039]

Further, the volatile organic compound adsorbent of the
15 present invention contains the pores of micro sizes that are distributed densely and homogeneously therein, and it is expected that the active sites (e.g., solid acid points) possessed by the MFI type zeolite are also distributed densely and homogeneously. That is, the volatile organic compound
20 adsorbent of the present invention can be used as a catalyst for which the MFI type zeolite is, usually, used, such as acid catalyst, disproportionation catalyst, isomerization catalyst, catalyst for synthesizing hydrocarbons, catalyst for FCC, catalyst for polymerizing olefins and denitrating catalyst, or
25 as a catalyst carrier without any limitation.

EXAMPLES

[0040]

The invention will now be described using the following
30 Experimental Examples.

In the experiments, various measurements were taken by the methods described below.

[0041]

(1) X-ray diffraction

35 (Measurements and conditions for the analysis of spacing

d-values)

A dry sample was put into a desiccator of which the interior has been adjusted to be a relative humidity of 75%, and was left to stand still at room temperature for not less than 48 hours so as to adsorb the water to its amount of saturation. The sample was taken out and was measured for its X-ray diffraction over $2\theta = 29.6$ to 30.2° . The X-ray diffraction was measured by using the Ultima 4 manufactured by Rigaku Co. under the following conditions with Cu-K α .

10 Target: Cu
 Filter: Curved crystalline graphite monochrometer
 Detector: SC
 Voltage: 40 kV
 Current: 50 mA
 15 Step size: 0.005°
 Counting time: 10 sec/step
 Slit: DS2/3 $^\circ$ RS0.3 mm SS2/3 $^\circ$

In the X-ray diffraction over a desired range, a d-value ($\text{\AA}$) was found for an angle that showed a maximum peak according to the following formula.

(Bragg's conditions)

$$d = n\lambda / 2 \sin \theta$$

d: spacing

n: integer

25 λ : wavelength

$\sin \theta$: angle subtended by crystal plane and X-ray

(Confirming the type of crystal)

The crystal was confirmed by changing the following conditions out of the conditions used for the measurement of the d-value.

30 Measuring range: 3 to 40°
 Current: 40 mA
 Step size: 0.02°
 Counting time: 0.6 sec/step

35 [0042]

(2) Measuring the isothermal line of nitrogen adsorption

Nitrogen adsorptions were measured by using the Tristar manufactured by Micrometrics Co., and an isothermal line of adsorption was found in a range of a nitrogen partial pressure $P_{N_2}(P/P_0)$ of 0.005 to 0.95. The pretreatment was conducted in vacuum under the conditions of 200°C for 2 hours. The adsorbents that will be described later were measured for their nitrogen-adsorbing capabilities (cm^3/g) under a nitrogen partial pressure $P_{N_2}(P/P_0)$ of 0.005.

10 [0043]

(3) Measuring the isothermal line of toluene adsorption

Toluene adsorptions were measured by using the Belsorp Max manufactured by Microtrac BEL Co., and an isothermal line of adsorption was found in a range of a toluene partial pressure $P_T(P/P_0)$ of 0.0001 to 0.10. The pretreatment was conducted in vacuum under the conditions of 150°C for 2 hours. The time for judging the equilibrium was 300 seconds. The toluene was of the chromatograph grade produced by FUJIFILM Wako Pure Chemical Co. The adsorbents that will be described later were measured under a toluene partial pressure $P_T(P/P_0)$ of 0.01, and the measured values were converted into the amounts of adsorption per a unit mass of the adsorbent, and were regarded to be the toluene-adsorbing capabilities (% by mass).

[0044]

25 (4) Analysis of composition

Elemental analysis necessary for calculating the contents of alkali metals as oxides thereof and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratios), was conducted by using the Rigaku ZSX Primus II manufactured by Rigaku Co. Measurements were taken by using the target of Rh, the analysis line of $K\alpha$ and under the below-mentioned conditions.

30

The samples were those that were dried at 110°C for 2 hours.

Table 1

Element	Tube voltage kV	Tube current mA	Detector	Analyzing crystal
Si	30	100	PC	PET
Al	30	100	PC	PET
Na	30	100	PC	RX25

[0045]

(5) Measuring the median diameter (D50%)

5 The median diameters (μm) on the volume basis were measured by using a laser diffraction-type grain size distribution measuring apparatus, i.e., Mastersizer 3000, manufactured by Malvern Panalytical and using water as a solvent.

[0046]

10 (6) BET specific surface area

The specific surface areas were calculated from the isothermal line of adsorption found in (2) above relying on the BET method.

[0047]

15 (Comparative Example 1)

Use was made of the SILTON MT-100 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 105$) that was the MFI type zeolite produced by Mizusawa Industrial Chemicals, Ltd. The SILTON is a registered trademark of Mizusawa Industrial Chemicals, Ltd.

20 [0048]

(Comparative Example 2)

Use was made of the HSZ890HOA that was the MFI type zeolite produced by TOSOH Co.

[0049]

25 (Comparative Example 3)

Use was made of the ABSCENTS-3000 that was the MFI type zeolite produced by Union Showa Co.

[0050]

(Comparative Example 4)

(Preparation of silica hydrogel)

A silica hydrogel was prepared by a conventional method by using 40% by mass of sulfuric acid and No. 3 sodium silicate
5 (SiO₂ = 22.8% by mass, Na₂O = 7.6% by mass, H₂O = 69.6% by mass). The composition was analyzed to be SiO₂ = 38.5% by mass, Na₂O = 0.02% by mass and H₂O = 61.4% by mass.

(Synthesis of the MFI type zeolite)

10 Into a 2-liter stainless steel jug, there were put silica hydrogel, TPA-Br, 49% by mass of NaOH and water in such amounts that the mass of the SiO₂ was 200 g and that the mole ratios of the components were SiO₂:Na₂O:TPA-Br:H₂O = 1:0.025:0.045:16. The components were mixed at room temperature with stirring to prepare a mixed gel thereof.

15 Next, the mixed gel was transferred to a 1.5-liter autoclave incorporating a stirrer blade therein, was heated up to 170°C over a period of 2.5 hours with stirring and was, thereafter, put to the crystallization reaction for 12 hours while maintaining the temperature of 170°C. After the reaction
20 has been finished, the liquid was filtered and was then washed with water of a volume 3 times as large as the volume of the mixed gel to thereby obtain an MFI type zeolite containing template. The MFI type zeolite after filtered and washed with water possessed a median diameter of 10.0 μm.

25 The MFI type zeolite was dried on a constant-temperature drying rack heated at 110°C for 10 hours, and from which the template was removed in a Muffle furnace under the conditions of 600°C for 2 hours to obtain an MFI type zeolite free of template.

30 (Pulverizing the MFI type zeolite)

The MFI type zeolite was pulverized by using a swirl type jet mill. The powder after pulverized possessed a median diameter of 7.7 μm.

[0051]

35 (Example 1)

A mixed gel was prepared in the same manner as in Comparative Example 4 but setting the mass of the SiO_2 to be 200 g and changing the composition of the components to be at mole ratios of $\text{SiO}_2:\text{Na}_2\text{O}:\text{TPA-Br}:\text{H}_2\text{O} = 1:0.03:0.05:16$. Finally, seed crystals (MFI type zeolite having a median diameter of 7.7 μm obtained in Comparative Example 4) were added in an amount of 1.0% by mass relative to the SiO_2 , and the mixture thereof was, further, stirred for 5 minutes to prepare a mixed gel containing seed crystals.

Next, the mixed gel containing the seed crystals was heated in a temperature controllable hot-water bath up to 95°C over one hour with stirring, and was subjected to the crystallization reaction for 20 hours maintaining the temperature of 95°C. After the reaction, the reaction solution was filtered and was then washed with water of a volume three times as much as the volume of the mixed gel to thereby obtain an MFI type zeolite containing the template. The MFI type zeolite after filtered and washed with water possessed a median diameter of 1.0 μm .

The MFI type zeolite was dried on the constant-temperature drying rack heated at 110°C for 10 hours, and from which the template was removed in the Muffle furnace under the conditions of 600°C for 2 hours to obtain an MFI type zeolite free of template. Thereafter, the MFI type zeolite was pulverized by using the swirl type jet mill in the same manner as in Comparative Example 4 to obtain a volatile organic compound adsorbent comprising the MFI type zeolite. The adsorbent possessed a median diameter of 1.0 μm .

[0052]

(Example 2)

To 10 g of the volatile organic compound adsorbent comprising the MFI type zeolite of Example 1, there was added 90 g of water so that the adsorbent was dispersed therein again with stirring. Thereafter, 10 g of ammonium chloride was added thereto to carry out an exchange treatment for 3 hours. After

filtered and washed with water, the obtained ammonium-MFI type zeolite was dried on the constant-temperature drying rack heated at 110°C for 10 hours, and from which the ammonium was removed in the Muffle furnace under the conditions of 500°C for 3 hours to obtain an MFI type zeolite from which the alkali has been removed. The zeolite was pulverized again by using the swirl type jet mill to obtain a volatile organic compound adsorbent comprising the MFI type zeolite. The adsorbent possessed a median diameter of 1.0 μm .

10 [0053]

(Example 3)

A volatile organic compound adsorbent comprising an MFI type zeolite was obtained in the same manner as in Example 1 but using a 1.5-liter autoclave incorporating a stirrer as the reaction vessel, and conducting the reaction at 105°C for 16 hours. The adsorbent possessed a median diameter of 2.0 μm .

[0054]

(Example 4)

20 A volatile organic compound adsorbent comprising an MFI type zeolite was obtained in the same manner as in Example 1 but changing the composition of the mixed gel to be at mole ratios of $\text{SiO}_2:\text{Na}_2\text{O}:\text{TPA-Br}:\text{H}_2\text{O} = 1:0.025:0.045:16$, using the 1.5-liter autoclave incorporating a stirrer as the reaction vessel, and conducting the reaction at 110°C for 18 hours. The adsorbent possessed a median diameter of 4.0 μm .

25 [0055]

(Example 5)

A mixed gel containing seed crystals was prepared by using a sodium aluminate ($\text{Al}_2\text{O}_3 = 23.0\%$ by mass, $\text{Na}_2\text{O} = 19.2\%$ by mass, $\text{H}_2\text{O} = 57.8\%$ by mass) in addition to using the starting materials shown in Example 1, mixing them together at room temperature with stirring such that the composition of the mixed gel thereof was at mole ratios of $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{TPA-Br}:\text{H}_2\text{O} =$
30 1:0.008:0.05:0.04:16, and finally adding the seed crystals (MFI

type zeolite having the median diameter of $7.7\ \mu\text{m}$ obtained in Comparative Example 4) in an amount of 1.0% by mass relative to the SiO_2 . Thereafter, a volatile organic compound adsorbent comprising the MFI type zeolite was obtained in the same manner as in Example 1 but using the 1.5-liter autoclave incorporating the stirrer as the reaction vessel, and conducting the reaction at 120°C . The adsorbent possessed a median diameter of $1.8\ \mu\text{m}$.

[0056]

10 (Example 6)

A mixed gel containing seed crystals was prepared by setting the mass of the SiO_2 to be 380 g, using the MFI type zeolite having the median diameter of $1.0\ \mu\text{m}$ obtained in Example 1 as seed crystals in an amount of 3.0% by mass, and mixing together with stirring the starting materials inclusive of the seed crystals such that the composition of the components were at mole ratios of $\text{SiO}_2:\text{Na}_2\text{O}:\text{TPA-Br}:\text{H}_2\text{O} = 1:0.03:0.045:20$. The operations thereafter were conducted in the same manner as in Example 1 to obtain a volatile organic compound adsorbent comprising an MFI type zeolite. The adsorbent possessed a median diameter of $0.7\ \mu\text{m}$.

[0057]

(Example 7)

A mixed gel containing seed crystals was prepared by using the same starting materials as those used in Example 5, setting the mass of the SiO_2 to be 240 g, using the MFI type zeolite having the median diameter of $0.7\ \mu\text{m}$ obtained in Example 6 as seed crystals in an amount of 2.0% by mass, and mixing together with stirring the starting materials inclusive of the seed crystals such that the composition of the components was at mole ratios of $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{TPA-Br}:\text{H}_2\text{O} = 1:0.0077:0.12:0.04:20.3$. The operations thereafter were conducted in the same manner as in Example 1 but conducting the crystallization reaction for 48 hours to obtain a volatile organic compound adsorbent comprising an MFI type zeolite. The adsorbent possessed a

median diameter of 0.5 μm .

[0058]

5 The MFI type zeolites of Comparative Examples 1 to 4, and volatile organic compound adsorbents prepared in Examples 1 to 7 were tested for their properties, nitrogen-adsorbing capabilities and toluene-adsorbing capabilities. The results were as shown in Tables 2 and 3.

Table 2

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
Toluene-adsorbing capability ($P/P_0 = 0.01$)	Mass %	8.9	9.7	8.6	8.4	8.9	8.9	8.4
d-Value, plane (053)	Å	2.980	2.988	2.987	2.980	2.987	2.984	2.986
N ₂ -adsorbing capability ($P/P_0 = 0.005$)	cm ³ /g	108	109	103	105	104	103	103
Alkali metal content as oxide	Mass %	0.70	0.04	0.67	0.44	1.21	0.43	1.59
SiO ₂ /Al ₂ O ₃ (mole ratio)	-	11900	6660	8060	5720	112	6740	95
Grain size (D50%)	μm	1.0	1.0	2.0	4.0	1.8	0.7	0.5
BET specific surface area	m ² /g	457	450	440	435	456	440	468

Table 3

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Toluene-adsorbing capability ($P/P_0 = 0.01$)	Mass %	8.1	7.3	6.0	6.7
d-Value, plane (053)	Å	2.991	2.992	2.991	2.991
N ₂ -adsorbing capability ($P/P_0 = 0.005$)	cm ³ /g	96	93	89	95
Alkali metal content as oxide	Mass %	1.71	ND	1.28	0.34
SiO ₂ /Al ₂ O ₃ (mole ratio)	-	105	1800	949	4980
Grain size (D50%)	μm	3.7	-	-	7.7
BET specific surface area	m ² /g	420	405	365	380

[0061]

Applied Example; Preparation of a resin composition blended with the adsorbent

The pelletized polyethylene (product name; LF440B)
5 produced by Japan Polypropylene Co. was mixed with the adsorbent of Example 6, and the mixture thereof was melt-kneaded by using the LABO PLASTOMILL manufactured by Toyo Seiki Mfg. Co., at 170 °C and was cut into chips to obtain a resin composition containing the adsorbent in an amount of 0.5 parts per 100 parts
10 by mass of the resin. No other components were added than the adsorbent.

[0062]

Evaluating the capability for adsorbing the resin odor;

Capabilities for reducing the resin odor were evaluated
15 by using the resin compositions blended with the adsorbent obtained in the above preparation of the resin compositions and by using the pelletized polyethylene without containing the adsorbent.

5 Grams of each of the resin composition blended with the
20 adsorbent and the pelletized polyethylene without containing the adsorbent were put into 500-mL screw cap bottles. A Teflon tape was wound three times on the screw portions of the bottles and, thereafter, a cap was fitted thereto to seal. The bottles were provided for each of the panelists (for five persons). The
25 bottles containing the pelletized polyethylene were introduced into the constant-temperature drying rack preheated at 50°C, and were left to stand at 50°C for 90 hours. The bottles of the two kinds were then taken out from the constant-temperature drying rack, and were opened to immediately let the panelists
30 smell the odor and evaluate the degree of odor (0: does not smell at all, 1: faintly smells, 2: smells). The test was conducted without letting the panelists know in which bottle the pellets were contained. The results of test were as shown in Table 4.

[0063]

Table 4

Adsorbent	Degree of odor	
	Example 6	Blank
Panelist 1	1	2
Panelist 2	1	2
Panelist 3	1	2
Panelist 4	1	2
Panelist 5	1	2
Average	1	2

CLAIMS

[Claim 1]

A volatile organic compound adsorbent including an MFI type zeolite

wherein the zeolite having:

an $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratio) of not less than 50;

a spacing (d-value) on a plane (053) of not more than 2.99 Å in an X-ray diffraction spectrum;
a BET specific surface area of not less than 430 m^2/g ; a nitrogen-adsorbing capability of not less than 100 (cm^3/g) under a nitrogen partial pressure P_{N_2} (P/P_0) of 0.005; and a toluene-adsorbing capability of not less than 8.2 mass% under a toluene partial pressure P_{T} (P/P_0) OF 0.01.

[Claim 2]

The adsorbent according to claim 1, wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (mole ratio) is not less than 90.

[Claim 3]

The adsorbent according to any one of claims 1 to 2, wherein the content of an alkali metal calculated as an oxide thereof is suppressed to be not more than 0.1% by mass.

[Claim 4]

A resin composition obtained by blending a resin with the adsorbent of any one of claims 1 to 3.

[Claim 5]

The resin composition according to claim 4, wherein said adsorbent is contained in an amount of 0.005 to 100 parts by mass per 100 parts by mass of said resin.

[Claim 6]

The resin composition according to claim 4, wherein said resin is a thermoplastic resin.