

## SPECIFICATION

### TITLE OF THE INVENTION

METHOD FOR RECOVERING STYRENE MONOMER FROM  
POLYSTYRENE RESIN BY USING A CATALYST

### BACKGROUND OF THE INVENTION

#### Technical Field of the Invention

The present invention relates to a method for recovering styrene monomers from a polystyrene resin by using a catalyst, and its objective is to provide a method for recovering styrene monomers from polystyrene resin wastes at comparatively low temperatures with high yield.

### PRIOR ART

Polystyrene resins are one type of industrial plastics which were developed earliest among thermoplastic resins, and since they are superior in moldability and inexpensive, they have been used in a wide range of applications.

Among these, foamed polystyrenes, which have been widely used as packaging materials for electric appliances, AV apparatuses, etc., cushioning materials for fix boxes, glass products, etc. and trays and heat insulating and cold reserving containers for food, etc., are bulky and are not decomposed even if they are buried in the soil; therefore, it is difficult to prepare a site for disposal. Moreover, since they have high burning temperatures, they tend to damage incinerators, and since they produce dioxin when mixed with a chlorine-containing material, it is difficult to

dispose them through incineration; thus, they have raised major problems in industrial waste disposal.

Under such circumstances, a number of arts for recovering aromatic hydrocarbon oils such as styrene monomers from polystyrene resins have been proposed, and examples of them include those arts disclosed in JP No. 283745/1996 (Tokukaihei 8-283745), JP No. 221681/1997 (Tokukaihei 9-221681) and JP No. 302356/1997 (Tokukaihei 9-302356).

Any of these arts thermally decompose polystyrene resins under the presence of a catalyst; however, since the thermal decomposing process is carried out by heating polystyrene resins to high temperatures of 350 to 430° C, special plant facilities resistant to high temperatures are required, and such investments for facilities have increased initial costs.

Moreover, since recovered oils contain many components other than styrene monomers, the yield of styrene monomers becomes very low; for example, in the case of the method of JP No. 283745/1996, the ratio of styrene monomers contained in the recovered oils is as low as approximately 68 to 69 %.

Here, JP No. 2545768 has disclosed a method for recovering styrene monomers from polystyrene resins by applying a heating process in a comparatively low temperature range of 300 to 350° C; however, even by the application of this method, the content of the styrene monomers contained in the recovered oils is in the range of 60 to 79 %, which fails to achieve a satisfactory level.

## BRIEF SUMMARY OF THE INVENTION

The present invention has been devised to solve the above-mentioned problems, and its objective is to provide a method for recovering styrene monomers from polystyrene resins by using a catalyst, which can thermally decompose polystyrene resins at a comparatively low temperature so that it is possible to reduce the facility costs, etc., and which can recover oils that have less ratio of low molecular weight components and a high content of styrene monomers from the thermally decomposed vapor.

The present invention has been devised to solve the above-mentioned problems, and the invention according to claim 1 relates to a method for recovering styrene monomers from a polystyrene resin by using a catalyst, which obtains the styrene monomers by thermally decomposing the polystyrene resin, and which is characterized in that a sulfate is used as the catalyst.

The invention according to claim 2, which relates to the method of claim 1 for recovering styrene monomers from a polystyrene resin by using a catalyst, wherein the sulfate is a metal sulfate.

The invention according to claim 3, which relates to the method of claim 1 for recovering styrene monomers from a polystyrene resin by using a catalyst, wherein the sulfate is at least one member selected from the group consisting of magnesium sulfate, sodium sulfate, iron sulfate, manganese sulfate, zinc sulfate, aluminum sulfate, calcium sulfate, potassium sulfate and antimony sulfate.

The invention according to claim 4, which uses the method of claim 1 for recovering styrene monomers from a polystyrene resin by using a catalyst,

wherein the heating temperature of the polystyrene resin is set to not more than 350° C.

### PREFERRED EMBODIMENTS OF THE INVENTION

Referring to FIG.s, the following description will discuss preferred embodiments of a method for recovering styrene monomers from polystyrene resin by using a catalyst in accordance with the present invention.

FIG. 1 is a schematic view that shows one example of a thermal decomposing device used in the present invention.

The thermal decomposing device (1) is constituted by a decomposing vessel (2) which houses material polystyrene resins (for example, polystyrene resin lumps having a fixed shape formed by air-releasing and pulverizing foaming polystyrene resins) inside thereof and thermally decomposes them, a supply section (3) for supplying the polystyrene resins to the decomposing vessel (2), a vapor outlet section (4) which externally releases thermally decomposed vapors generated in the decomposing vessel (2), a stirring device (5) for stirring and mixing the contents loaded inside the decomposing vessel (2), and a heating means, not shown.

Here, the device shown in FIG. 1 only schematically shows one example of the device used in the method of the present invention, and the device used in the method of the present invention is not intended to be limited thereby.

Polystyrene resins having a fixed shape formed by air-releasing and pulverizing, for example, foaming polystyrene are continuously supplied from the supply section (3) to the decomposing vessel (2), and to this decomposing

vessel (2) is added a catalyst for accelerating thermal decomposition of the polystyrene resins.

The present invention is characterized by using a sulfate as this catalyst. Specifically, examples thereof include: zinc sulfate, aluminum sulfate, antimony sulfate, antimony (III) sulfate, ammonium sulfate, ammonium aluminum sulfate, ammonium chromium (III) sulfate, ammonium cobalt (II) sulfate, ammonium iron (II) sulfate, ammonium iron (III) sulfate, ammonium manganese (II) sulfate, iridium (III) sulfate, lead sulfate, lead sulfate ore, cadmium sulfate, potassium sulfate, gallium (III) sulfate, potassium aluminum sulfate, potassium chromium (III) sulfate, calcium sulfate, normal silver sulfate, guanidinium aluminum sulfate, chromium (II) sulfate, chromium (III) sulfate, cobalt (II) sulfate, cobalt (III) sulfate, zirconium (IV) sulfate, mercury (I) sulfate, hydrogen 3-indryl sulfate, hydrogen potassium sulfate, tin (II) sulfate, strontium sulfate, cerium (III) sulfate, cerium (IV) sulfate, titanium (III) sulfate, titanium (IV) sulfate, iron (II) sulfate, iron (III) sulfate, copper (II) sulfate, dodecyl sodium sulfate, thorium (IV) sulfate, sodium sulfate, sodium aluminum sulfate, lead (II) sulfate, lead (IV) sulfate, nickel (II) sulfate, nickel (II) aluminum sulfate, nitrosyl sulfate, disodium magnesium sulfate, neodymium (III) sulfate, vanadium (III) sulfate, barium sulfate, hydroxyl ammonium sulfate, praseodymium (III) sulfate, magnesium sulfate, magnesium dipotassium sulfate, manganese (II) sulfate, manganese (III) sulfate, lanthanum (III) sulfate, lignin sulfate, lithium sulfate, rubidium sulfate, rubidium aluminum sulfate, manganese (III) cesium sulfate.

Moreover, the following hydrates of these sulfates may be used: zinc

sulfate monohydrate, zinc sulfate hexahydrate, zinc sulfate heptahydrate, aluminum sulfate hexahydrate, aluminum sulfate decahydrate, aluminum sulfate 16-hydrate, aluminum sulfate 18-hydrate, aluminum sulfate 27-hydrate, ammonium chromium (III) sulfate 12-hydrate, ammonium cobalt (II) sulfate hexahydrate, ammonium iron (II) sulfate hexahydrate, ammonium iron (III) sulfate 12-hydrate, ammonium manganese (II) sulfate hexahydrate, cadmium sulfate monohydrate, cadmium sulfate  $8/3$ -hydrate, cadmium sulfate heptahydrate, cadmium aluminum 24-hydrate, potassium aluminum sulfate 12-hydrate, potassium aluminum sulfate 16-hydrate, potassium chromium (III) sulfate 12-hydrate, potassium chromium (III) sulfate hexahydrate, potassium chromium (III) sulfate trihydrate, potassium chromium (III) sulfate monohydrate, calcium sulfate dihydrate, chromium (II) sulfate heptahydrate, chromium (III) sulfate 18-hydrate, chromium (III) sulfate trihydrate, cobalt (II) sulfate hexahydrate, cobalt (II) sulfate monohydrate, cobalt (III) sulfate 18-hydrate, zirconium (IV) sulfate monohydrate, zirconium (IV) tetrahydrate, cerium (III) sulfate octahydrate, cerium (IV) sulfate tetrahydrate, titanium (IV) sulfate tetrahydrate, iron (III) sulfate monohydrate, iron (II) sulfate tetrahydrate, iron (II) sulfate pentahydrate, iron (II) sulfate heptahydrate, iron (III) sulfate trihydrate, iron (III) sulfate hexahydrate, iron (III) sulfate heptahydrate, iron (III) sulfate 7.5-hydrate, iron (III) sulfate nonahydrate, iron (III) sulfate decahydrate, iron (III) sulfate 12-hydrate, copper (II) sulfate pentahydrate, thorium (IV) sulfate dihydrate, thorium (IV) sulfate tetrahydrate, thorium (IV) sulfate hexahydrate, thorium (IV) sulfate octahydrate, thorium (IV) sulfate nonahydrate, sodium sulfate heptahydrate, sodium sulfate decahydrate,

sodium aluminum sulfate 24-hydrate, nickel (II) sulfate monohydrate, nickel (II) sulfate dihydrate, nickel (II) sulfate tetrahydrate, nickel (II) sulfate heptahydrate, disodium magnesium sulfate 2.5-hydrate, disodium magnesium tetrahydrate, vanadium (II) sulfate heptahydrate, vanadium (III) sulfate trihydrate, vanadium (III) sulfate nonahydrate, magnesium sulfate monohydrate, magnesium sulfate 1.5-hydrate, magnesium sulfate dihydrate, magnesium sulfate trihydrate, magnesium sulfate hexahydrate, magnesium sulfate heptahydrate, magnesium dipotassium sulfate tetrahydrate, magnesium dipotassium sulfate hexahydrate, manganese (II) sulfate monohydrate, manganese (II) sulfate dihydrate, manganese (II) sulfate tetrahydrate, manganese (II) sulfate pentahydrate, manganese (II) sulfate heptahydrate, and manganese (III) cesium sulfate 12-hydrate.

Among the above-mentioned sulfates, metal sulfates are preferably used, and among the metal sulfates, magnesium sulfates, sodium sulfates, iron sulfates, manganese sulfates, zinc sulfates, aluminum sulfates, calcium sulfates, potassium sulfates, antimony sulfates, and hydrates of these sulfates are more preferably used.

One kind of these catalysts may be used, or two or more kinds of these may be used in combination.

Moreover, the above-mentioned catalyst, as it is, may be added, or the above-mentioned catalyst supported on a carrier may be added. With respect to the carrier, although not particularly limited, those superior in heat resistance, such as glass fiber, silica, alumina and titanium oxide, are preferably used.

With respect to the method for allowing the carrier to support the

catalyst, it is not particularly limited; and a known method such as a dipping method and a co-precipitation method may be used.

Moreover, with respect to the shape of the catalyst, the catalyst may have a lump shape, a powder form or another shape; and those having a particle size of approximately 0.3 to 3.0 mm are preferably used.

In the present invention, the amount of the catalyst to be added is set in the range of 10 to 25 weight %, and more preferably, 10 to 20 weight %.

The amount of addition of the catalyst less than 10 weight % fails to sufficiently exert the functions and effects of the application of the catalyst, and the amount thereof exceeding 25 weight % also fails to exert the corresponding effects, giving adverse effects on production costs.

Next, the following description will discuss one example of a method for recovering styrene monomers from polystyrene resins by using a catalyst in accordance with the present invention.

First, a polystyrene resin as a material (for example, air-released foaming polystyrene resin) is loaded inside the decomposing vessel (2) in the thermal decomposing device (1), and the above-mentioned catalyst is added to the inside of the decomposing vessel (2).

Next, this is heated while being mixed and stirred by the stirring device (5) so that the polystyrene resin is allowed to contact the catalyst so as to be thermally decomposed.

The heating temperature of the polystyrene resin, which is determined depending on the kinds of a catalyst to be used, is preferably set in the range of 230 to 350° C, more preferably, 250 to 330° C.

More specifically, for example, the preferable heating temperature

ranges for the respective catalysts are shown as follows: in the case of magnesium sulfate, the temperature range is 230 to 330° C, in the case of iron sulfate, the temperature range is 200 to 310° C, in the case of sodium sulfate, the temperature range is 250 to 330° C. In the case of manganese sulfate, the temperature range is 200 to 350° C, in the case of zinc sulfate, the temperature range is 200 to 350° C, in the case of aluminum sulfate, the temperature range is 210 to 310 ° C, in the case of calcium sulfate, the temperature range is 220 to 310° C, in the case of potassium sulfate, the temperature range is 300 to 350° C, and in the case of antimony sulfate, the temperature range is 250 to 310° C.

Thermally decomposed vapors generated by the application of heat are taken out of the thermal decomposing device (1) through the vapor outlet section (4).

Then, the thermally decomposed vapors, taken out of the device is condensed and liquefied to obtain crude styrene monomer, and this crude styrene monomer is vacuum-distilled to recover a styrene monomer with high purity.

### Examples

The following description will discuss the method for recovering styrene monomers from polystyrene resins by using a catalyst of the present invention by means of examples so as to clarify the effects of the present invention. However, the present invention is not intended to be limited by these examples.

(Example 1)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 2.

To a flask (9) were loaded 80 g of polystyrene resin and 8g of magnesium sulfate heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and this was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15).

Thermally decomposed vapors generated in the flask are condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The amount of the liquid collected in the collecting bin (13) was 72.91 g (recovery: 91.14 %), and the components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 90.0156 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.5394 % and 0.8776% respectively. Here, FIG. 3 is a chart showing the results of the gas chromatography analyses, and FIG. 4 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 240 to 260 ° C, and the thermally decomposed vapor temperature was 145 to 147° C.

Then, the recovered liquid was vacuum-distilled so that styrene monomer having a purity of 99.92 % which satisfies the purity of 99.5 %

conforming to JIS standard was obtained.

(Example 2)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 50 g of polystyrene resin and 9.65 g of magnesium sulfate ( $\text{MgSO}_4$ ) calcined at  $500^\circ\text{C}$ , and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5\text{ mm}$ , made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto. The heating process by this ribbon heater was made so as to preliminarily heat the path from the outlet of the flask to the cooling tube to not less than  $145^\circ\text{C}$ ; thus, it became possible to prevent the initially distilled portion of the vapor taken out from the outlet of the flask from being liquefied and again dropping inside the flask before reaching the cooling tube.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask (9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 96.1607 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 1.9955 % and 0.2363% respectively. Here, FIG. 6 is a chart showing the results of the gas chromatography analyses, and FIG. 7 show numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 257 to 334 ° C, and the thermally decomposed vapor temperature was 159.0 to 199.6° C.

(Example 3)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of magnesium sulfate ( $\text{MgSO}_4$ ) calcined at 800° C, and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi$  5 mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as

#### Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 94.5081 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.4536 % and 0.3544% respectively. Here, FIG. 8 is a chart showing the results of the gas chromatography analyses, and FIG. 9 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 306.5 to 324.9° C, and the thermally decomposed vapor temperature was 154.8 to 203.3° C.

#### (Example 4)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 60 g of polystyrene resin and 15 g of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring

blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 89.4618 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.2737 % and 5.4044% respectively. Here, FIG. 10 is a chart showing the results of the gas chromatography analyses, and FIG. 11 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 286 to 328° C, and the thermally decomposed vapor temperature was 210 to 234.6° C.

#### (Example 5)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 80 g of polystyrene resin and 20 g of iron sulfate ( $\text{FeSO}_4$ ), and a net plate (16) was placed at an upper position inside the

flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 92.9584 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.5875 % and 0.7139 % respectively. Here, FIG. 12 is a chart showing the results of the gas chromatography analyses, and FIG. 13 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 192.0 to 306.5° C, and the thermally decomposed vapor temperature was 157.7 to 261.4° C.

#### (Example 6)

A thermal decomposing process of polystyrene resin was carried out

through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of manganese sulfate ( $\text{MnSO}_4$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 96.6863 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 1.8501 % and 0.3731 % respectively. Here, FIG. 14 is a chart showing the results of the gas chromatography analyses, and FIG. 15 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 200.8 to 340.2° C, and the thermally decomposed

vapor temperature was 145.4 to 180.4° C.

(Example 7)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of zinc sulfate ( $\text{ZnSO}_4$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 92.1085 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 3.3474 % and 0.8941 % respectively. Here, FIG. 16 is a chart showing the results of the

gas chromatography analyses, and FIG. 17 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 196.0 to 351.2° C, and the thermally decomposed vapor temperature was 146.3 to 241.3° C.

(Example 8)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were

analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 95.0094 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.0112 % and 0.9381 % respectively. Here, FIG. 18 is a chart showing the results of the gas chromatography analyses, and FIG. 19 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 202.3 to 304.3° C, and the thermally decomposed vapor temperature was 145.7 to 172.4° C.

#### (Example 9)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of calcium sulfate ( $\text{CaSO}_4$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 94.3744 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.7867 % and 0.4139 % respectively. Here, FIG. 20 is a chart showing the results of the gas chromatography analyses, and FIG. 21 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 211.6 to 303.8° C, and the thermally decomposed vapor temperature was 146.3 to 197.5° C.

#### (Example 10)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 100 g of polystyrene resin and 20 g of potassium sulfate ( $K_2SO_4$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics, were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14)

and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 90.4612 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.5724 % and 1.3448 % respectively. Here, FIG. 22 is a chart showing the results of the gas chromatography analyses, and FIG. 23 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 301.3 to 350.6° C, and the thermally decomposed vapor temperature was 148.6 to 178.7° C.

#### (Example 11)

A thermal decomposing process of polystyrene resin was carried out through the following method by using an experimental device as shown in Fig. 5.

To a flask (9) were loaded 50 g of polystyrene resin and 10 g of antimony sulfate ( $\text{Sb}_2(\text{SO}_4)_3$ ), and a net plate (16) was placed at an upper position inside the flask (9), and Raschig rings of  $\phi 5$  mm, made of ceramics,

were put onto the net plate (16) so as to form a filled substance layer (17).

This was subjected to a heating process by heating the inside of the flask (9) by a mantle heater (11) while being mixed and stirred by stirring blades (10); and the liquid temperature was measured by a thermometer (14) and the outlet temperature of thermally decomposed vapors was measured by a thermometer (15). Here, a ribbon heater (not shown) was wound around the outlet of the flask (9) so as to apply heat thereto in the same manner as Example 2.

Thermally decomposed vapors generated in the flask were condensed and liquefied by a cooling tube (12) connected to the outlet of the flask(9), and the resulting liquid was collected into a collecting bin (13).

The components of the recovered liquid in the collecting bin (13) were analyzed by gas chromatography; and the results show that the content of styrene monomers is as high as 90.8510 %, and the contents of toluene and ethylbenzene, which are low-molecular components, are as low as 2.1073 % and 0.2313 % respectively. Here, 24 shows numeric value data of the results of the gas chromatography analyses.

Here, with respect to temperatures while the liquid had being distilled, the liquid temperature was 250.6 to 301.3° C, and the thermally decomposed vapor temperature was 149.1 to 185.8° C.

As described above, the method for recovering styrene monomers from polystyrene resins by using a catalyst of the present invention makes it possible to recover oil containing less ratio of low molecular weight components such as toluene and ethylbenzene and a high content of styrene monomers from vapors obtained through thermal decomposition of

polystyrene resins.

Moreover, the present method makes it possible to thermally decompose polystyrene resins at comparatively low temperatures for a short time, and to reduce catalyst costs; thus, it is possible to provide styrene monomers with high production efficiency.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view showing one example of a thermal decomposing device used in the present invention.

FIG. 2 is a schematic view showing one example of an experimental device used in Example 1 of the present invention.

FIG. 3 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 1.

FIG. 4 shows numeric data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 2.

FIG. 5 is a schematic view showing one example of an experimental device used in Examples 2 through 11 of the present invention.

FIG. 6 s a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 2.

FIG. 7 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 2.

FIG. 8 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 3.

FIG. 9 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 3.

FIG. 10 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 4.

FIG. 11 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 4.

FIG. 12 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 5.

FIG. 13 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 5.

FIG. 14 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 6.

FIG. 15 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 6.

FIG. 16 is a chart that shows the results of gas chromatography

analyses on distilled products (crude styrene monomers) obtained in Example 7.

FIG. 17 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 7.

FIG. 18 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 8.

FIG. 19 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 8.

FIG. 20 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 9.

FIG. 21 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 9.

FIG. 22 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 10.

FIG. 23 shows numeric value data of the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example 10.

FIG. 24 is a chart that shows the results of gas chromatography analyses on distilled products (crude styrene monomers) obtained in Example

11.

## CLAIMS

What is claimed is:

1. A method for recovering styrene monomers from a polystyrene resin by using a catalyst, which obtains the styrene monomers by thermally decomposing the polystyrene resin, wherein a sulfate is used as the catalyst.
2. The method for recovering styrene monomers from a polystyrene resin by using a catalyst according to claim 1, wherein the sulfate is a metal sulfate.
3. The method for recovering styrene monomers from a polystyrene resin by using a catalyst according to claim 1, wherein the sulfate is at least one member selected from the group consisting of magnesium sulfate, sodium sulfate, iron sulfate, manganese sulfate, zinc sulfate, aluminum sulfate, calcium sulfate, potassium sulfate and antimony sulfate.
4. The method for recovering styrene monomers from a polystyrene resin by using a catalyst according to claims 1, wherein the heating temperature of the polystyrene resin is set to not more than 350° C .

