



(86) Date de dépôt PCT/PCT Filing Date: 2001/04/12
(87) Date publication PCT/PCT Publication Date: 2001/11/01
(45) Date de délivrance/Issue Date: 2006/08/29
(85) Entrée phase nationale/National Entry: 2001/12/19
(86) N° demande PCT/PCT Application No.: JP 2001/003172
(87) N° publication PCT/PCT Publication No.: 2001/080993
(30) Priorité/Priority: 2000/04/20 (JP2000-119648)

(51) Cl.Int./Int.Cl. *B01J 23/42* (2006.01),
B01D 53/86 (2006.01), *B01J 23/44* (2006.01)
(72) Inventeurs/Inventors:
TOKURA, KATSUHIRO, JP;
OSHITA, KAZUYUKI, JP
(73) Propriétaire/Owner:
NGK INSULATORS, LTD., JP
(74) Agent: OGILVY RENAULT LLP/S.E.N.C.R.L., S.R.L.

(54) Titre : ELABORATION D'UN CATALYSEUR DE DECOMPOSITION POUR HALOGENURE ORGANIQUE ET
PROCEDE DE FABRICATION DE FILTRE DESTINE A LA DECOMPOSITION D'HALOGENURE ORGANIQUE
(54) Title: METHOD FOR PREPARING DECOMPOSITION CATALYST FOR ORGANIC HALIDE AND METHOD FOR
MANUFACTURING FILTER FOR USE IN DECOMPOSING ORGANIC HALIDE

(57) **Abrégé/Abstract:**

An organic halogen compound-decomposing catalyst is provided, which affords excellent decomposing percentages even at low temperatures, while there is no fear of re-synthesizing dioxines and brominated dioxines. An organic halogen compound-decomposing catalyst is obtained by reacting a Pt salt and/or a Pd salt, an alkoxide derivative of Ti compound and an amino acid as an organic binder in a solvent, thereby synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof, and heating the organic metal precursor. This catalyst may be carried on a surface of a clean side of a ceramic filter. Since active points can be increased by uniformly dispersing the Pt and/or Pd particles in Ti particles, the catalyst has higher activity as compared with those obtained by conventional processes, and can exhibits excellent decomposing effects even at lower than 200°C.



Abstract of the Disclosure

An organic halogen compound-decomposing catalyst is provided, which affords excellent decomposing percentages even at low temperatures, while there is no fear of re-synthesizing dioxines and brominated dioxines.

An organic halogen compound-decomposing catalyst is obtained by reacting a Pt salt and/or a Pd salt, an alkoxide derivative of Ti compound and an amino acid as an organic binder in a solvent, thereby synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof, and heating the organic metal precursor. This catalyst may be carried on a surface of a clean side of a ceramic filter. Since active points can be increased by uniformly dispersing the Pt and/or Pd particles in Ti particles, the catalyst has higher activity as compared with those obtained by conventional processes, and can exhibit excellent decomposing effects even at lower than 200°C.

SPECIFICATION

METHOD FOR PREPARING DECOMPOSITION CATALYST FOR ORGANIC HALIDE AND METHOD FOR MANUFACTURING FILTER FOR USE IN DECOMPOSING ORGANIC HALIDE

Technical Field

The present invention relates to a process for producing organic halogen compound-decomposing catalysts to be used in treating waste gases mainly from incinerators, and a process for producing organic halogen compound-decomposing filters.

Background Art

There are improvements in burning conditions and advancements in waste gas treatment to reduce organic halogen compounds generated from city garbage incinerators. In general, high temperatures of not lower than 1000°C are required to be maintained to completely oxidize and decompose halogenated organic substances such as organic halogen compounds in burning processes, but burning temperatures are usually set at 800 to 900°C to prevent damages of furnace walls. It is not easy to completely oxidize and decompose the organic halogen compounds represented by organic chlorine compounds through improvements in burning conditions.

In a stoker furnace where a low-temperature area or an incompletely burning area tends to be locally formed, a re-burning section needs to be provided to completely oxidize and decompose the organic halogen compounds. However, this poses problems in that the total amount of waste gases increases, and running costs with a re-burning fuel rises.

It is known that among the organic halogen compounds, dioxines and brominated dioxines are produced not only in the burning process, but also such are synthesized again from non-pyrolised and unburnt residual portions and benzene ring-possessing precursor materials over a wide temperature zone of around 300 to 500°C. Therefore, even if the dioxines and the brominated dioxines are tried to be reduced in the burning process, such are synthesized again in a succeeding stage. Consequently, the dioxines and the brominated dioxines in the waste gases are sometimes not reduced.

For the above reasons, the organic halogen compounds in the waste gases, including the dioxines and the brominated dioxines, need to be removed through the waste gas treatment so that they may be kept stably at low concentrations.

Adsorption methods : adsorption with activated carbon and decomposition with a catalyst are recited for the removal of the organic halogen compounds in the waste gases, including the dioxines and the brominated dioxines through the waste gas treatment. Although the adsorption method is the mainstream in the existing treatment of the organic halogen compounds, it is costly, and poses a problem in that activated carbon having adsorbed the dioxines becomes a secondary waste, which causes a post treatment problem thereof. On the other hand, although the catalytically decomposing method has a merit that no secondary waste is produced, it has problems in that the dioxines are synthesized again through secondary reactions with the catalyst and the catalyst is degraded.

Although denitrifying catalysts of a V_2O_5 - TiO_2 system and a V_2O_5 - WO_3 - TiO_2 system have been formerly used as organic chloride compound-decomposing catalysts, it has been confirmed that the dioxines are produced contrary to expectation particularly if the concentration of the dioxines at an inlet for the catalyst is low. In recent years, there are not few areas where the concentration of the dioxines in the waste gases is suppressed to not more than 1/10 times the standard level set by the government by residential agreements or the like. Thus, the re-synthesis of the dioxines with the catalyst becomes a problem. Further, since such a conventional catalyst needs to be used at high temperatures of 200 to 500°C, a problem that the waste gases need to be heated again comes out.

Moreover, investigations and researches have been recently more actively made on the levels of influences upon human health of the dioxines and the brominated dioxines produced during the burning processes of the wastes and the treating processes of the waste gases as well as on processes through which they are produced.

Having thus examined the re-synthesis phenomena of the dioxines and the brominated dioxines with the catalysts, the inventors confirmed that V_2O_5

causes the above, and that if Pt and/or Pd is used, catalysts which decompose organic halogen compounds including the dioxines and the brominated dioxines can be obtained, free from the re-synthesis problem. A method which is ordinarily considered to produce titanium in which Pt and/or Pd is dispersed is a method of coating a powder of titanium oxide with an aqueous solution of a Pt salt and/or a Pd salt or impregnating a sintered body thereof with this solution, heating the resultant, decomposing the salt(s) and thereby precipitating Pt and/or Pd thereon.

In the organic halogen compound-decomposing catalyst obtained by this method, however, the Pt and/or Pd particles have large diameters, and precipitate on the surface of titanium oxide uniformly. Thus, there is a problem that an catalytic effect is not effectively exhibited if the particle diameters of titanium oxide are small. In addition, the titaniumoxide particles are sintered, and titanium oxide and noble metal particles are simultaneously grain-grown (sintered), if the particles are heated at high temperatures. It causes degradation in the catalytic activity.

Problems to Be Solved by the Invention

The present invention has been accomplished to provide a process for producing an organic halogen compound-decomposing catalyst which can solve the above-mentioned problems of the prior art, increase active points by uniformly dispersing Pt and/or Pd fine particles in titanium particles, and assuredly oxidize and decompose the organic halogen compounds including the dioxines and the brominated dioxines, without fear of synthesizing the dioxines and the brominated dioxines again, even if the catalytic reaction temperature is lowered to 200°C or less.

It is another object of the present invention to provide a process for producing an organic halogen compound-decomposing filter by using the above organic halogen compound-decomposing catalyst.

Countermeasures to solve the problems

The process for producing the organic halogen compound-decomposing catalyst according to the present invention, which process has been made to solve the above problems, comprises the steps of synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof by reacting a Pt

salt and/or a Pd salt, an organic Ti compound and an organic binder in a solvent, heating the organic metal precursor, and thereby obtaining the organic halogen compound-decomposing catalyst in which fine particles of Pt and/or Pd are dispersed in TiO_2 .

The process for producing an organic halogen compound-decomposing filter according to the present invention, comprises the steps of synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof by reacting a Pt salt and/or a Pd salt, an organic Ti compound, and an organic binder in a solvent, coating the organic metal precursor on a surface of a clean side of a ceramic filter or coating the precursor on wall surfaces of inner pores of the filter by impregnation, heating the resulting filter, and thereby carrying on the ceramic filter the organic halogen compound-decomposing catalyst in which fine particles of Pt and/or Pd are dispersed in TiO_2 .

In the organic halogen compound-decomposing catalyst obtained by the process of the present invention, the Pt and/or Pd fine particles are dispersed in the TiO_2 by heating the organic metal precursor containing Pt and/or Pd and Ti in its molecules. Therefore, as compared with conventional catalysts obtained by coating or impregnation, the catalyst of the present invention has largely increased active points, and can be highly activated. Thus, the amount of expensive Pt or Pd can be reduced to cut the cost. The organic metal precursor is ordinarily heated at a heating temperature of 450 to 500°C in an air atmosphere under atmospheric pressure. The heating time is set at such a sufficient length in connection with the heating temperature, etc. that the organic binder is completely burnt out and that Pt or Pd is uniformly dispersed in TiO_2 . Further, since the organic halogen compound can be decomposed even under a low temperature condition of less than 200°C, the waste gases need not be heated again, and the organic halogen compound is not synthesized again. In the present invention, "Pt or Pd" means "Pt and/or Pd".

In the organic halogen compound-decomposing filter obtained by the process of the present invention, the organic halogen compound-decomposing catalyst having such functions is carried on the surface of the clean side of the ceramic filter or on the inner filtering wall surfaces of the filter. Thus, the filter has a merit that dust is removed with simultaneous decomposition of the organic

halogen compounds.

Embodiments of working the Invention

In the following, preferred embodiments of each of the inventions will be shown.

First, an organic compound of Ti, and a soluble salt of Pt and/or Pd are dissolved in a solvent containing an organic binder. As the Ti organic compound, an alkoxide derivative (for example, a derivative in which a part of the Ti alkoxide is replaced by acetyl acetate group(s) or a derivative in which a part of the Ti alkoxide is replaced by triethanol amine group(s)) may be used. As the soluble Pt salt, chloroplatinic acid, chloroplatinic acid hexahydrate, platinum dichloride, platinum tetrachloride or the like may be used. As the soluble Pd salt, palladium chloride, palladium nitrate or the like may be used.

As the organic binder for Ti and the noble metal(s), an amino acid such as L-lysine, L-glycine or L-proline may be used. Particularly, L-proline is preferred, because it has a high solubility in methanol to be used as the solvent. Ti ions are bonded to Pt and/or Pd ions by the organic binder, which fixes the ions in the molecules. As the organic Ti compound, the Ti alkoxide derivative is preferably used.

The "organic binder" is a material which fixes the Ti ions and the Pt and/or Pd ions in the molecules of the organic binder through bonding the above ions with the binder, is removed by heating and thus produces bound fine particles of TiO_2 and Pt and/or Pd. The material does not give adverse influences such as catalytic poison upon the physical properties of the organic halogen compound-decomposing catalyst.

A preferred mixing ratio of the above components is that the Pt and/or Pd salt is 0.5 to 5 wt. parts, methanol is 100 to 200 wt. parts, and amino acid is 0.1 to 1.5 wt. parts relative to 100 wt. parts of the organic Ti compound (for example, the Ti alkoxide derivative). When these components are reacted at 70°C to 80°C, an organic metal precursor in which the components are uniformly dispersed as considered at a molecular level. The organic metal precursor means that the Ti ions and the Pt and/or Pd ions are connected to each other in one molecule via chemical bonds. Different from a case where such ions are dissolved in a solvent, relative positional relationship among these ions is fixed.

In this state, Ti is bound with Pt and/or Pd via the amino acid. When the precursor is heated to 450 to 500°C, however, the amino acid as the organic binder is burnt out, the organic metal precursor is thus decomposed, the Pt and/or Pd is converted to super fine particles and highly dispersed in TiO₂ produced through oxidation of Ti, and the organic halogen compound-decomposing catalyst in which Pt and/or Pd is around 1 to 10 wt. parts relative to 100 wt. parts of TiO₂ can be obtained.

Since the active points of the organic halogen compound-decomposing catalyst are increased by converting the Pt and/or Pd to the super fine particles, the catalytic activity is improved. Owing to this, the use amount of Pt and/or Pd can be reduced, and the lower cost can be realized, as compared with the prior art. Furthermore, since the catalyst has a performance of decomposing the organic halogen compounds even at low temperatures of less than 200°C, it has many merits, e.g., that the waste gases need to be heated again. As described in examples mentioned later, the decomposing efficiency of the dioxines with this catalyst is much higher than a catalyst obtained by a method in which a titanium oxide powder is coated with an aqueous solution of a Pt salt and/or a Pd salt, and Pt and/or Pd is precipitated by heating and decomposing.

In one embodiment of the invention in which the organic binder is an amino-acid, the above organic metal precursor is not heated as it is, but the precursor is converted to a catalyst-coating solution by mixing it with a TiO₂ sol functional as a glue, and is coated on the surface of a clean side of a porous ceramic filter, followed by heating. As a result, the halogen compound-decomposing catalyst in which Pt and/or Pd is converted to super fine particles and highly dispersed in TiO₂ can be carried on the clean side of the ceramic filter. Alternatively, the inner pore wall surfaces of the ceramic filter can be coated by immersing the filter into the above catalyst-coating solution and heating the resultant filter.

When the ceramic filter is used for the treatment of the waste gases, dust can be filtered off with the ceramic filter, and the organic halogen compounds in the waste gases can be simultaneously decomposed with the organic halogen compound-decomposing catalyst. Further, since the organic halogen compound-decomposing catalyst is carried on the clean side of the filter or on the inner pore wall surfaces of the filter, the catalyst can be prevented from

being degraded with the dust contained in the waste gases. Furthermore, while the organic halogen compounds in the waste gases are decomposed when they pass the filter walls containing the catalyst, the flow rate of the waste gases increases when they pass the pores in the filter walls. Thus, the decomposition is promoted due to the dispersing effect as compared with common catalysts in the form of a honeycomb and pellets having no filtering function.

Besides, the organic halogen compound-decomposing catalyst can be carried on an activated carbon adsorbent by coating the adsorbent with the catalyst-coating solution of the organic metal precursor or impregnating the solution into the adsorbent. The use temperature limit of the activated carbon adsorbent is 130 to 150°C, but the organic halogen compound-decomposing catalyst according to the present invention can exhibit a sufficient dioxine-decomposing effect even in such a low temperature range. Therefore, when this activated carbon adsorbent is used for the treatment of the waste gases, it can adsorb the organic halogen compounds and the catalyst can oxidize and decompose the compounds, so that not only the organic halogen compounds can be decomposed, but also heavy metals, SO₂, HCl, etc. can be removed through adsorption.

Examples

(Example 1)

In order to confirm the effects of the present invention mentioned above, orthochlorotoluene, which was considered as a substituting material for the dioxines in the catalytic engineering, was used, and its oxidation decomposing percentage was measured.

What was used in an experiment was an organic halogen compound-decomposing catalyst which was produced by mixing 1 wt. part of Pt with 100 wt. parts of an alkoxide derivative of Ti, dissolving the mixture into methanol containing an amino acid, impregnating the surface of a ceramic honeycomb filter with the resulting precursor solution at a rate of Pt being 1 g/l volume liter honeycomb, and heating the honeycomb filter. For a comparison purpose, a

ceramic honeycomb filter was prepared through being impregnated with a conventional dioxine-decomposing catalyst, followed by heating. The catalyst had been prepared by coating a powder of titanium oxide having a specific surface area of $70 \text{ m}^2/\text{g}$ with Pt, and the impregnation rate was identically 1 g Pt/1 volume liter honeycomb.

These two kinds of the honeycombs were set in an equipment where a waste gas containing orthochlorotoluene and CO was flown under conditions of SV of 8000h^{-1} and a temperature of 190°C , and their decomposing percentages were measured. As a result, CO could be decomposed at around 98% in each of the catalyst produced from the precursor solution according to the present invention and the catalyst obtained in Comparative Example, so that no conspicuous difference was seen with respect to the CO oxidation decomposing percentage. However, the orthochlorotoluene oxidation decomposing percentage as the substituting material for the dioxines was over 75% in the catalyst according to the present invention, but about 50% in the case of the catalyst of the comparative example. This confirmed the superiority of the present invention in a low temperature range of less than 200°C .

(Example 2)

The above Example was an example conducted, bearing in mind the organic chlorine compound including the dioxines. On the other hand, orthobromotoluene was used, bearing in mind the organic bromo compound including the brominated dioxines as other organic halogen compounds, and its oxidation decomposing percentage was measured.

What was used in an experiment was an organic halogen compound-decomposing catalyst which was produced by mixing 1 wt. part of Pt with 100 wt. parts of an alkoxide derivative of Ti, dissolving the mixture into methanol containing an amino acid, impregnating the surface of a ceramic honeycomb filter with the resulting precursor solution at a rate of Pt being 1 g/l volume liter honeycomb, and heating the honeycomb filter. For a comparison purpose, a ceramic honeycomb filter was prepared through being impregnated with a conventional dioxine-decomposing catalyst, followed by heating. The catalyst had been prepared by coating a powder of titanium oxide having a specific surface area of $70 \text{ m}^2/\text{g}$ with Pt, and the impregnation rate was identically 1 g

Pt/1 volume liter honeycomb.

These two kinds of the honeycombs were set in an equipment where a waste gas containing orthobromotoluene and CO was flown under conditions of SV of 8000h^{-1} and a temperature of 190°C , and their decomposing percentages were measured. As a result, CO could be decomposed at around 98% in each of the catalyst produced from the precursor solution according to the present invention and the catalyst obtained in Comparative Example, so that no conspicuous difference was seen with respect to the CO oxidation decomposing percentage. However, the orthobromotoluene oxidation decomposing percentage as the substituting material for the dioxines was over 70% in the catalyst according to the present invention, but about 40% in the catalyst of Comparative Example. This confirmed the superiority of the present invention in a low temperature range of less than 200°C .

(Example 3)

An experiment was effected in the same manner as in Example 1 except that a carrying amount of Pt was changed, and the temperature of a honeycomb catalyst portion was 190°C . That is, Pt was mixed at 0.25, 0.5, 1, 5 or 10 g/1 liter honeycomb, and TiO_2 mixed at 100 g/1 liter honeycomb. Almost no changes were seen with respect to the orthochlorotoluene-removing percentage in a range of 1 to 10 g/1 liter honeycomb. However, since the noble metal is expensive, not more than 1 g/1 liter honeycomb is preferable from the view of the cost.

(Example 4)

With respect to the experimental method in Example 1 under the conditions of $\text{SV}8000\text{h}^{-1}$, 200°C and Pt/Pd and TiO_2 being mixed at 1g/1 liter honeycomb and 100g/1 liter honeycomb, respectively, a CO-decomposing percentage and an orthochlorotoluene-decomposing percentage (O-CT decomposing percentage) and an orthobromotoluene-decomposing percentage (O-BT decomposing percentage) when the orthobromotoluene was used instead of orthochlorotoluene were measured according to the process of Example 1 and the conventional method in which a conventional dioxine-decomposing catalyst having titanium oxide powder having a specific surface area of $70\text{ m}^2/\text{g}$ coated with Pt was similarly impregnated at 1 g Pt, Pd/1 volume liter honeycomb,

followed by heating. As compared with the conventional process, the invention process exhibited far more excellent CO-decomposing percentage, O-CT decomposing percentage and O-BT decomposing percentage, and that Pd gave similar test results as in the case of Pt.

(Effects of the Invention)

As explained above, in accordance with the various embodiments of the invention, the organic halogen compound-decomposing catalyst of which active points are increased by uniformly dispersing the fine particles of Pt and/or Pd in titania particles by utilizing the organic metal precursor can be obtained. Since this catalyst can assuredly oxidize and decompose the organic halogen compounds even if the catalyst reaction temperature is lowered to 200°C or less, the waste gases need not be heated again unlike the conventional methods. In addition, different from the conventional V_2O_5 - TiO_2 based catalyst and V_2O_5 - WO_3 - TiO_2 based catalyst, there is no fear of synthesizing the dioxines again even if the concentration of the catalyst at the inlet is low. According to one embodiment of the invention in which the organic binder is an amino-acid, the ceramic filter can be obtained, which can simultaneously remove dust and decompose the organic halogen compounds by carrying on the ceramic filter the organic halogen compound-decomposing catalyst in which the Pt and/or Pd fine particles are dispersed in Ti.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing an organic halogen compound-decomposing catalyst, comprising the steps of:

- synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof by reacting 0.5 - 5 parts by weight of a Pt salt and/or a Pd salt, 100 parts by weight of an organic Ti compound and 0.1 - 1.5 parts by weight of an organic binder in 100 – 200 parts by weight of a solvent; and
- heating the organic metal precursor to form an organic halogen compound-decomposing catalyst containing fine particles of Pt and/or Pd dispersed in TiO_2 .

2. A process according to claim 1, wherein said organic binder comprises an amino acid.

3. A process according to claim 1, wherein said organic Ti compound comprises an alkoxide derivative of Ti.

4. A process for producing an organic halogen compound-decomposing filter, comprising the steps of;

- synthesizing an organic metal precursor containing Pt and/or Pd and Ti in molecules thereof by reacting 0.5 – 5 parts by weight of a Pt salt and/or a Pd salt, 100 parts by weight of an organic Ti compound and 0.1 – 1.5 parts by weight of an organic binder in 100 – 200 parts by weight of a solvent;
- coating the organic metal precursor on a surface of a clean side of a ceramic filter or coating the precursor on wall surfaces of inner pores thereof by impregnation; and

- heating the resulting filter to form an organic halogen compound-decomposing catalyst on said filter, said catalyst containing fine particles of Pt and/or Pd dispersed in TiO_2 .

5. A process according to claim 4, wherein said organic binder comprises an amino acid.

6. A process according to claim 3, wherein said organic Ti compound comprises an alkoxide derivative of Ti.