



(11) **EP 1 595 864 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:  
**27.05.2015 Bulletin 2015/22**

(51) Int Cl.:  
**B01J 37/20** (2006.01) **C07C 309/62** (2006.01)  
**B01J 31/02** (2006.01) **B01J 31/06** (2006.01)  
**C07C 309/38** (2006.01)

(21) Application number: **03815739.2**

(86) International application number:  
**PCT/JP2003/011442**

(22) Date of filing: **08.09.2003**

(87) International publication number:  
**WO 2004/069789 (19.08.2004 Gazette 2004/34)**

(54) **POLYCYCLIC AROMATIC HYDROCARBON BASED SOLID STRONG ACID**

AUF POLYZYKLISCHEM AROMATISCHEM KOHLENWASSERSTOFF BASIERENDE STARKE FESTKÖRPERSÄURE

ACIDE FORT SOLIDE À BASE D'HYDROCARBURES AROMATIQUES POLYCYCLIQUES

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **05.02.2003 JP 2003027810**

(43) Date of publication of application:  
**16.11.2005 Bulletin 2005/46**

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**WO-A1-98/30519 JP-A- 63 097 624**  
**US-A- 1 711 449**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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**Description**

## FIELD OF THE INVENTION

5 [0001] The present invention relates to a solid acid insoluble in a polar solvent obtained by a process characterizing that polycyclic aromatic hydrocarbon or polycyclic aromatic hydrocarbon to which carbon material is blended is heat-treated in conc. sulfuric acid or in fuming sulfuric acid, then the polycyclic aromatic hydrocarbon is condensed and sulfonated, or composed with carbon materials which is blended at the condensation or sulfonation reaction, or a composite solid strong acid composed by said solid acid and carbon material and an use of said solid acid as a solid strong acid catalyst.

## DESCRIPTION OF THE PRIOR ART

15 [0002] Currently, energy situations or environmental situations are in critical situation, and it is required to produce only a subjected product alone effectively by small energy without producing unnecessary by product. Acid catalyst is necessary for chemical industries of the present age, and used in production of various products such as chemicals, products of petrochemical industry or polymer products, and considerable parts of the acid catalysts are a liquid acid such as hydrochloric acid or sulfuric acid. The liquid acid catalyst used in a production process is separated from the product and recovered by means of processes of neutralization with a base and removal of salt which is formed by the neutralization. However, energy consumed for the neutralization process and the removal process of salt occupies considerable parts in total energy used in all production processes. And the recovered salts are over supply in a market, further, since mostly of these salts are by-products whose utilizability is small, in many cases, treatment of these salts are difficult.

20 [0003] In such a circumstance, a solid acid does not need said neutralization process or removing process of salt for separation and recovery, does not form unnecessary by-products and can produce an objected product by lower energy. Therefore, investigation was carried out in early stage (Ishihara, K; Hasegawa, A; Yamamoto, H. Angew. Chem. Int. Ed.2001, 40, 4077; Document 1). As the results of the investigation, a solid acid catalyst such as zeolite, silica alumina or hydrous niobate obtains good results in chemical industries and provides good benefit to human society. Further, as a strong acid polymer, material prepared by sulfonation of polystyrene can be considered as a solid acid and has been used as a cationic ion-exchange resin which indicates acidity for a long time. Furthermore, Nafion (T.M. of Du-pont) which loads sulfone group on polytetrafluoroethylene skeleton is known as a very strong solid acid (solid super strong acid) having hydrophilicity, and it is well known that these acid polymers act as a super strong acid having acid strength stronger than liquid acid. However, polymer has problems that it is weak to heat and is too expensive for an industrial use. Accordingly, from the view points of performance and cost, it is very difficult to design more advantageous industrial process by using solid acid catalyst than industrial process using liquid acid catalyst, therefore, almost all chemical industries depend on liquid acid catalyst. Considering said circumstance, development of a solid acid catalyst that exceeds a liquid acid catalyst from view points of performance and cost has been desired.

30 [0004] Further, as an inorganic type, although sulfuric acid trace zirconia prepared by sulfuric acid treatment of zirconium oxide ( $ZrO_2$ ) is a solid acid catalyst having the strongest acidity, the amount of sulfuric acid trace is not so large, and numbers of acid point per unit weight is smaller than that of liquid acid, therefore, it is hard to satisfy said requirement.

35 [0005] The subject of the present invention is to provide a solid acid catalyst which dissolves said problems and can be advantageously usable for an industrial use. The inventors of the present invention think about a structure characterizing that sulfuric groups are loaded to a chemical material possessing a basic backbone which is stable against physical action such as heat, and pay attention to use a polycyclic hydrocarbon compounds characterizing that many aromatic compound rings, which are contained in tar, pitch, fuel oil or asphalt, are condensed as a composing material of said basic backbone. The inventors of the present invention use tar, pitch, fuel oil or asphalt itself or a polycyclic hydrocarbon compounds characterizing that many aromatic compound rings are condensed as a composing material of said basic backbone, heat treated them in concentrated sulfuric acid or fuming sulfuric acid, and the chemical structural feature and acid characteristic of the obtained product are investigated, and found out that condensation reaction of the composing material of said basic backbone is progressed simultaneously with sulfonation and an useful material as a solid acid which can be used stable in high temperature condition can be obtained. Further, the inventors of the present invention carried out esterification reaction of ethylalcohol and acetic acid by trial, and find out that said reaction is remarkably accelerated by presence of said solid acid and is useful as a solid acid catalyst, thus the subject can be accomplished. Further, in an investigation to obtain a solid acid material which improves the characteristics of said obtained solid acid, carbon materials such as activated carbon or acetylene black are blended to the material of said solid acid and heat treated in concentrated sulfuric acid or fuming sulfuric acid, and find out that a composite solid acid of polycyclic aromatic carbon solid acid-carbon material can be obtained.

## SUMMARY OF THE INVENTION

**[0006]** The present invention provides a method of condensing and sulphonating polycyclic aromatic hydrocarbons, comprising heat treating polycyclic aromatic hydrocarbons in concentrated sulphuric acid or fuming sulphuric acid at a temperature T of  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$ , to thereby prepare a solid acid which is insoluble in a polar solvent, wherein the polycyclic aromatic hydrocarbons are selected from naphthalene, anthracene, perylene, coronene and mixtures thereof, tar, pitch, fuel oil and asphalt containing a polycyclic aromatic hydrocarbon in which two or more aromatic rings are condensed. Preferably, the temperature T for heat treatment is  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$ .

**[0007]** The present invention also provides a solid acid obtainable by such a method.

**[0008]** The present invention further provides a method of condensation and sulfonation which method comprises heat treating a blend of polycyclic aromatic hydrocarbons and a carbon material in concentrated sulphuric acid or fuming sulphuric acid at a temperature of T of from  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$  to provide a composite solid strong acid which is insoluble in a polar solvent, wherein the polycyclic aromatic hydrocarbons are selected from naphthalene, anthracene, perylene, coronene and mixtures thereof, tar, pitch, fuel oil and asphalt containing a polycyclic aromatic hydrocarbon in which two or more aromatic rings are condensed and wherein the carbon material is at least one selected from carbon black, acetylene black, activated carbon, carbon nano tube and fullerene. Preferably, the temperature T for heat treatment is  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$ .

**[0009]** The present invention additionally provides a composite solid strong acid obtainable by such a method.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]**

Fig. 1 shows catalytic activity of a solid acid obtained in Example 1 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid (● catalyst is existing, ■ without catalyst. These marks are same in Figs 2-5).

Fig.2 shows catalytic activity of a solid acid obtained in Example 2 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.3 shows catalytic activity of a solid acid obtained in Example 3 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig. 4 shows catalytic activity of a solid acid obtained in Reference Example 4 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.5 shows catalytic activity of a solid acid obtained in Example 5 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.6 shows catalytic activity of a solid acid obtained in Example 6 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid (● shows activity of first time use and ○ shows activity of 2<sup>nd</sup> time use. These marks are same in Figs 7-10).

Fig.7 shows catalytic activity of a solid acid obtained in Example 7 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.8 shows catalytic activity of a solid acid obtained in Example 8 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.9 shows catalytic activity of a solid acid obtained in Example 9 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig. 10 shows catalytic activity of a solid acid obtained in Example 10 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig.11 shows catalytic activity of an acid catalyst composed of SO<sub>3</sub>H type Nafion powder (product of Du pont) of Comparative Example 3 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

Fig. 12 shows catalytic activity of an acid catalyst composed of zirconia sulfate (product of Wako Junyaku) of Comparative Example 4 at first time use and 2<sup>nd</sup> time use.

Fig. 13 shows catalytic activity of an activated carbon treated by concentrated sulfuric acid (96%) of Comparative Example 5 when it is used as an acid catalyst for esterification reaction of ethanol and acetic acid.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

**[0011]** The present invention will be illustrated more in detail.

I. The acid catalyst of the present invention, which is insoluble in a polar solvent, can be obtained by heat treating polycyclic aromatic hydrocarbons selected from naphthalene, anthracene, perylene, coronene and mixtures thereof, and tar, pitch, fuel oil and asphalt containing a polycyclic aromatic hydrocarbon in which two or more aromatic rings

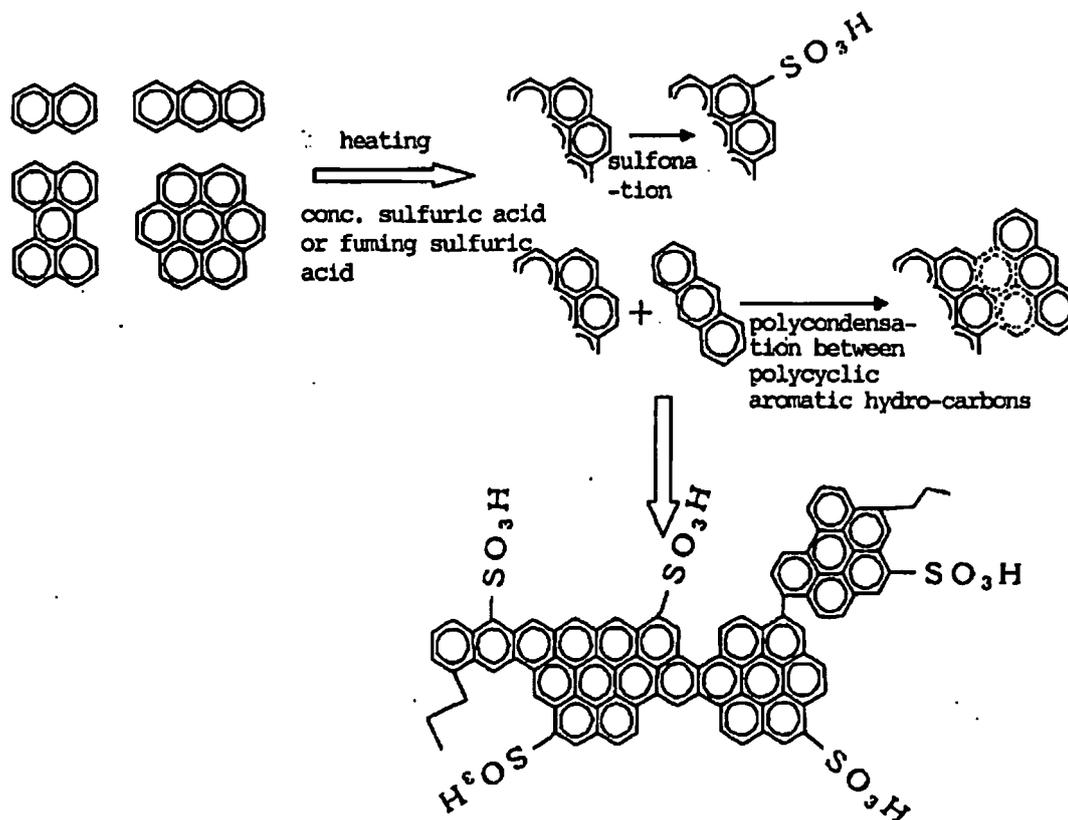
are condensed, in concentrated sulfuric acid or fuming sulfuric acid, and condensation reaction of said polycyclic aromatic hydrocarbons is progressed simultaneously with sulfonation reaction, therefore stabilized chemical structure is formed. Further, said solid acid indicates strong acidity and is useful as a solid strong acid catalyst and has a advantageous that it can be synthesized by lower cost.

As an example of a polar solvent in which said solid acid is insoluble, water, alcohol, aldehyde, carboxylic acid, ketone, amine or imine can be mentioned.

II. The polycyclic aromatic hydrocarbons referred to above are used as a starting material for synthesis of a solid acid of the present invention. When the degree of condensation is too small, the time for synthesis of solid acid becomes long. Therefore, it is desirable to use a compound characterized at least five aromatic rings are condensed as a starting material to obtain stable solid acid from the view point of industrial production.

**[0012]** It is well known that the polycyclic aromatic hydrocarbons are polycondensed in concentrated sulfuric acid or fuming sulfuric acid and an amorphous material characterized that polycyclic aromatic hydrocarbons are complexly polycondensed is formed. Further, its properties become closer to that of graphite along with the increase of the numbers of aromatic rings.

The inventors of the present invention, predict that polycyclic aromatic hydrocarbon characterized that many aromatic rings are condensed forms the structure which progressed to two dimensional shape similar to graphite, and even if the outermost aromatic rings are sulfonated, it becomes a solid acid which is insoluble in water based on the largely advanced structure of hydrophobic polycyclic aromatic hydrocarbon, and tried heat treatment indicated by following formula 1. Formula 1 indicates a concept of the present invention in a case that plural aromatic hydrocarbons are used as a starting material.



Formula 1

**[0013]** Said polycyclic aromatic hydrocarbon composed of naphthalene, anthracene, perylene or coronene is heat treated in concentrated sulfuric acid or fuming sulfuric acid and sulfonation and polycondensation reactions are carried out. By said sulfonation and polycondensation reactions, amorphous carbon material characterized that many sulfonated polycyclic aromatic hydrocarbons are condensed can be obtained.

**[0014]** The solid acid catalyst of the present invention can be synthesized using pitch, tar, fuel oil or asphalt in which various polycyclic aromatic hydrocarbons, saturated hydrocarbon or unsaturated hydrocarbon are contained or mixture

thereof as starting materials for synthesis.

**[0015]** The heat treatment is carried out at a temperature of from 200 to 450°C, preferably at from 200 to 350°C.

**[0016]** When treating temperature in concentrated sulfuric acid or fuming sulfuric acid is lower than 200°C, since polycondensation of the polycyclic aromatic hydrocarbon does not progress sufficiently and a polycyclic aromatic hydrocarbon composed of many aromatic rings is not formed, a solid acid which is insoluble in a polar solvent can not be obtained. On the contrary, when the treating temperature exceeds 450°C, insoluble amorphous hydro carbon in which sufficient amount of sulfone group to occur heat decomposition of sulfone group is existing.

**[0017]** More desirable heat treatment temperature is 200-350°C. The solid acid catalyst of the present invention can be synthesized not only by starting material composed of single polycyclic aromatic hydrocarbon but also by starting material composed of plural polycyclic aromatic hydrocarbons. Further, the solid acid catalyst of the present invention can be synthesized using pitch, tar, fuel oil or asphalt in which various polycyclic aromatic hydrocarbons, saturated hydrocarbon or unsaturated hydrocarbon are contained or mixture thereof as starting materials for synthesis.

III. As a carbon material used for the synthesis for a composite solid strong acid by blending with starting materials for synthesis of said polycyclic aromatic hydrocarbons, carbon black, acetylene black, activated carbon (granular state, whisker state, pulp state), graphite, carbon nano tube or fullerene, which are characterized to hold formed solid acid as a carrier for solid catalyst, desirably, a carbon material having surface structure to the surface of which many sulfate roots can be arranged, can be mentioned.

## EXAMPLE

**[0018]** The present invention will be illustrated more specifically according to the Examples, however, not intending to limit the scope of the present invention.

### Measuring Apparatus;

#### **[0019]**

A. Crystalline characteristic of synthesized solid acid catalyst is measured by an X-ray diffraction instrument, Geigerlex RAD-B, Cu K $\alpha$ , product of Rigaku Co., Ltd.

B. Elementary analysis, sulfur content is measured using CHNS-932, product of LECO Co., Ltd., by burning a specimen under oxygen gas flow. C. Stability of sulfone group is measured by temperature-programmed desorption (Multi Task TPD, product of Japan Bell Co., Ltd.) and thermogravimetric analysis (DTG-60/60H, product of Shimadzu Co., Ltd.).

#### Example 1

**[0020]** 1.00g of coronene (C<sub>24</sub>H<sub>12</sub>) is added to 100mL of conc. sulfuric acid (96%) and heated at 200°C for 8hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, then black solid powder is obtained. This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 1.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 210°C, and is understood that thermo stability of it is high. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.1. In Fig.1, for the comparison, formation of ethyl acetate by reaction without catalyst is also shown by time lapse. As shown in Fig.1, forming speed of ethyl acetate in the presence of synthesized catalyst is remarkably high, and it is understood that the synthesized material acts as a strong solid acid catalyst.

#### Example 2

**[0021]** 1.00g of coronene (C<sub>24</sub>H<sub>12</sub>) is added to 100mL of conc. sulfuric acid (96%) and heated at 300°C for 8 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 300°C, then black solid powder is obtained. This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl

alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 0.8 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 230°C, and is understood that thermo stability of it is high. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 1.0mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography Results are shown in Fig.2. In Fig.2, for the comparison, formation of ethyl acetate by reaction without catalyst is also shown by time lapse. As shown in Fig.2, forming speed of ethyl acetate in the presence of synthesized catalyst is remarkably high, and it is understood that the synthesized material acts as a strong solid acid catalyst.

#### Example 3

**[0022]** 0.50g of coronene (C<sub>24</sub>H<sub>12</sub>) and 0.20g of anthracene are added to 100mL of conc. sulfuric acid (96%) and heated at 300°C for 8 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 300°C, then black solid powder is obtained. This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 4.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 210°C, and is understood that thermo stability of it is high. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.3. In Fig.3, for the comparison, formation of ethyl acetate by reaction without catalyst is also shown by time lapse. As shown in Fig.3, forming speed of ethyl acetate in the presence of synthesized catalyst is remarkably high, and it is understood that the synthesized material acts as a strong solid acid catalyst.

#### Reference Example 4

**[0023]** 1.00g of coronene (C<sub>24</sub>H<sub>12</sub>) is poured into a flask with a reflux condenser in which 20mL of fuming sulfuric acid (SO<sub>3</sub>:25%) is contained and refluxed at 150 °C for 2 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, then black solid powder is obtained. This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis using CHNS-932, which is a product of LECO Co., Ltd., USA, sulfur content of this polycyclic aromatic carbon solid strong acid is 0.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 210°C, and is understood that thermo stability of it is high. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.4. In Fig.4, for the comparison, formation of ethyl acetate by reaction without catalyst is also shown by time lapse. As shown in Fig.4, forming speed of ethyl acetate in the presence of synthesized catalyst is remarkably high, and it is understood that the synthesized material acts as a strong solid acid catalyst.

#### Example 5

**[0024]** 2.00g of petroleum pitch is added to 100mL of conc. sulfuric acid (96%) and heated at 300°C for 8 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 300°C, then black solid powder is obtained. This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 3.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it

is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 210°C, and is understood that thermo stability of it is high. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.5. In Fig.5, for the comparison, formation of ethyl acetate by reaction without catalyst is also shown by time lapse. As shown in Fig.5, forming speed of ethyl acetate in the presence of synthesized catalyst is remarkably high, and it is understood that the synthesized material using petroleum pitch as a starting material acts as a strong solid acid catalyst.

#### Example 6

**[0025]** 20g of naphthalene is added to 300mL of conc. sulfuric acid (96%) and heated at 250°C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, then black solid powder of polycyclic aromatic carbon solid strong acid is obtained. This polycyclic aromatic carbon solid strong acid is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From X-ray diffraction pattern of the obtained insulating polycyclic aromatic carbon solid strong acid any structure is not observed, therefore, this material is understood to be an amorphous material. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 7.1 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 250°C, and is understood that thermo stability of it is high.

**[0026]** Above mentioned polycyclic aromatic carbon solid strong acid is evacuated at 150°C for 1 hour, then 0.2g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 10mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.6(a). In Fig.6, for the comparison, formation of ethyl acetate by reaction using same amount of SO<sub>3</sub>H Nafion as a catalyst is also shown by time lapse (b). As shown in the Figure, in the presence of the synthesized catalyst, formation speed of ethyl acetate is very fast and it is understood that the synthesized material is a solid acid catalyst having stronger acid strength than that of Nafion (●). After reaction, recovered material is washed, then used as a catalyst of same reaction. Results are shown in Fig.6 (○). As clearly understood from Fig.6, acid catalytic activity of polycyclic aromatic carbon solid strong acid does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned above is carried out. Catalytic activity of it is same as to the case of Fig.6. These results indicate that said polycyclic aromatic carbon solid strong acid is chemically stable and acid strength of it is not deteriorated even in hot water of 150°C.

#### Example 7

**[0027]** 10g of fuel oil (A fuel oil) is added to 300mL of conc. sulfuric acid (96%) and heated at 250°C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, and then black solid powder of polycyclic aromatic carbon solid strong acid is obtained. This polycyclic aromatic carbon solid strong acid is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From X-ray diffraction pattern of the obtained insulating polycyclic aromatic carbon solid strong acid any structure is not observed, therefore, this material is understood to be an amorphous material. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 8.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 230°C, and is understood that thermo stability of it is high.

**[0028]** Above mentioned polycyclic aromatic carbon solid strong acid is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.7 (a). In Fig.7, for the comparison, formation of ethyl acetate by reaction using same amount of SO<sub>3</sub>H Nafion as a catalyst is also shown by time lapse (b). As shown in the Figure, in the presence of the synthesized catalyst, formation speed of ethyl acetate is very fast and it is understood that the synthesized material is a solid acid catalyst having stronger acid strength than that of Nafion (●). After reaction, recovered material is washed, then used as a catalyst of same reaction. Results are shown in Fig.7 (○). As clearly understood from Fig.7, acid catalytic activity of polycyclic aromatic carbon solid strong acid does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned

above is carried out. Catalytic activity of it is same as to the case of Fig.7. These results indicate that said polycyclic aromatic carbon solid strong acid is chemically stable and acid strength of it is not deteriorated even in hot water of 150°C.

#### Example 8

**[0029]** 5g of asphalt is added to 300mL of conc. sulfuric acid (96%) and heated at 250 °C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, and then black solid powder of polycyclic aromatic carbon solid strong acid is obtained. This polycyclic aromatic carbon solid strong acid is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From X-ray diffraction pattern of the obtained insulating polycyclic aromatic carbon solid strong acid any structure is not observed, therefore, this material is understood to be an amorphous material. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 5.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid in atmosphere is 280°C, and is understood that thermo stability of it is high.

**[0030]** Above mentioned polycyclic aromatic carbon solid strong acid is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.8(a). In Fig.8, for the comparison, formation of ethyl acetate by reaction using same amount of SO<sub>3</sub>H Nafion as a catalyst is also shown by time lapse (b). As shown in the Figure, in the presence of the synthesized catalyst, formation speed of ethyl acetate is very fast and it is understood that the synthesized material is a solid acid catalyst having stronger acid strength than that of Nafion (●). After reaction, recovered material is washed, then used as a catalyst of same reaction. Results are shown in Fig.8 (○). As clearly understood from Fig.8, acid catalytic activity of polycyclic aromatic carbon solid strong acid does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned above is carried out. Catalytic activity of it is same as to the case of Fig.8. These results indicate that said polycyclic aromatic carbon solid strong acid is chemically stable and acid strength of it is not deteriorated even in hot water of 150°C.

#### Example 9;

**[0031]** Polycyclic aromatic carbon solid strong acid - carbon material composite 5g of naphthalene and 5g of activated carbon are added to 300mL of conc. sulfuric acid (96%) and heated at 250°C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, and then black solid powder of polycyclic aromatic carbon solid strong acid - carbon material composite is obtained. This aromatic carbon solid strong acid - carbon material composite is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 3.5 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid - carbon material composite in atmosphere is 230°C, and is understood that thermo stability of it is high.

**[0032]** Above mentioned polycyclic aromatic carbon solid strong acid - carbon material composite is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.9(a). In Fig.9, for the comparison, formation of ethyl acetate by reaction using same amount of SO<sub>3</sub>H Nafion as a catalyst is also shown by time lapse (b). As shown in the Figure, in the presence of the synthesized catalyst, formation speed of ethyl acetate is very fast and it is understood that the synthesized material is a solid acid catalyst having stronger acid strength than that of Nafion (●). Further, it is confirmed that the obtained polycyclic aromatic carbon solid strong acid - carbon material composite indicates stronger activity than that of polycyclic aromatic carbon solid strong acid whose starting material is naphthalene alone, and it is also confirmed that acid catalytic activity can be improved by adhering polycyclic aromatic carbon solid strong acid to the surface of activated carbon having broad surface area. After reaction, recovered material is washed, then used as a catalyst of same reaction. Results are shown in Fig.9 (O). As clearly understood from Fig.9, acid catalytic activity of polycyclic aromatic carbon solid strong acid - carbon material composite does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid - carbon material composite is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned above is carried out. Catalytic activity of it is same as to the case of Fig.9.

[0033] These results indicate that said polycyclic aromatic carbon solid strong acid - carbon material composite is chemically stable and acid strength of it is not deteriorated even in hot water of 150°C.

#### Example 10

[0034] 5g of naphthalene and 5g of acetylene black are added to 300mL of conc. sulfuric acid (96%) and heated at 250°C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, and then black solid powder of polycyclic aromatic carbon solid strong acid - carbon material composite is obtained. This aromatic carbon solid strong acid - carbon material composite is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 4.7 atm%, and presence of many sulfonic acid groups are detected. From the results of temperature-programmed desorption and thermogravimetric analysis, it is confirmed that the decomposition temperature of the polycyclic aromatic carbon solid strong acid - carbon material composite in atmosphere is 230°C, and is understood that thermo stability of it is high.

[0035] Above mentioned polycyclic aromatic carbon solid strong acid - carbon material composite is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig.10(a). In Fig.10, for the comparison, formation of ethyl acetate by reaction using same amount of SO<sub>3</sub>H Nafion as a catalyst is also shown by time lapse (b). As shown in the Figure, in the presence of the synthesized catalyst, formation speed of ethyl acetate is very fast and it is understood that the synthesized material is a solid acid catalyst having stronger acid strength than that of Nafion (●). Further, it is confirmed that the obtained polycyclic aromatic carbon solid strong acid - carbon material composite indicates stronger activity than that of polycyclic aromatic carbon solid strong acid whose starting material is naphthalene alone, and it is also confirmed that acid catalytic activity can be improved by adhering polycyclic aromatic carbon solid strong acid to the surface of acetylene black having broad surface area.

[0036] After reaction, recovered material is washed, and then used as a catalyst of same reaction. Results are shown in Fig. 10 (O). As clearly understood from Fig.10, acid catalytic activity of polycyclic aromatic carbon solid strong acid - carbon material composite does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid - carbon material composite is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned above is carried out. Catalytic activity of it is same as to the case of Fig.10. These results indicate that said polycyclic aromatic carbon solid strong acid - carbon material composite is chemically stable and acid strength of it is not deteriorated even in hot water of 150°C.

#### Comparative Example 1

[0037] 1.00g of coronene (C<sub>24</sub>H<sub>12</sub>) is added to 100mL of conc. sulfuric acid (96%) and heated at 50°C for 8 hours, then centrifuged by 3000rpm rotating speed for 30 minutes, however solid is not separated. It is considered that by the temperature condition of 50°C, polycondensation of aromatic rings is not sufficient and sulfonated polycyclic aromatic carbon solid strong acid can not be existed as an insoluble solid.

#### Comparative Example 2

[0038] 1.00g of coronene (C<sub>24</sub>H<sub>12</sub>) is added to 100mL of conc. sulfuric acid (96%) and heated at 500°C for 2 hours, and black solid powder is obtained.

[0039] This solid powder is washed by 300mL of ethyl alcohol, and the washing process is repeated until sulfuric acid contained in ethyl alcohol after washed becomes under detection limit of elementary analysis. Since from X-ray diffraction pattern of the obtained black powder, any structure is not observed, this material is understood to be amorphous. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid is 0.05 atm%. Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. The forming speed of ethyl acetate is not so much different from the state of without catalyst and is clearly understood that the synthesized material does not act as a solid acid catalyst. For the quantitative analysis of sulfur amount loaded to the surface, X-ray photoelectron spectroscopic spectrum of said black powder is measured, and from the result it become clear that sulfur is not exist on the surface. The reason why is considered as follows, that is, when temperature for treatment is too high, sulfone groups on surface are decomposed.

## Comparative Example 3

5 [0040] Proton exchanged SO<sub>3</sub>H Nafion powder (product of Du'pont) is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig. 11(a). Formation of ethyl acetate is progressed under the presence of Nafion. After reaction, recovered material is washed, and then used as a catalyst of same reaction. Results are shown in Fig. 11. As clearly understood from Fig. 11, acid catalytic activity of Nafion does not deteriorate by repeating use. Further, said synthesized polycyclic aromatic carbon solid strong acid is heated with distilled water in an autoclave of 150°C for 72hours and filtrated. This filtrated powder is evacuated for 1 hour at 150°C, then 0.2g of it is used as a catalyst and same reaction as mentioned above is carried out. As shown in Fig. 11, catalytic activity of it is remarkably deteriorated (b). These results indicates that the stability of Nafion is lower than that of said polycyclic aromatic carbon solid strong acid - carbon material composite and acid strength of Nafion deteriorate in water of 150°C.

## 15 Comparative Example 4

20 [0041] Zirconia sulfate (product of Wako Junyaku Co., Ltd.) is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography Results are shown in Fig. 12. Formation of ethyl acetate is progressed under the presence of zirconia sulfate (●). After reaction, recovered material is washed, and then used as a catalyst of same reaction. Results are shown in Fig.12 (O). As clearly understood by the Figure, acid catalytic activity of zirconia sulfate remarkably deteriorated by repeating use, and sulfuric acid trace on the surface of zirconia sulfate is unstable in water.

## 25 Comparative Example 5

30 [0042] 5g of activated carbon is added to 300mL of conc. sulfuric acid (96%) and heated at 250°C for 15 hours. Excess conc. sulfuric acid is removed by vacuum distillation at 250°C, and then black powder is obtained. This black powder is washed by 300mL of distilled water at 90°C, and the washing process is repeated until sulfuric acid contained in water after washed becomes under detection limit of elementary analysis. From elementary analysis, sulfur content of this polycyclic aromatic carbon solid strong acid - carbon material composite is confirmed to be smaller than 0.05 atm%. X-ray diffraction pattern of the obtained black powder is same as X-ray diffraction pattern of the activated carbon before heat treatment in conc. sulfuric acid.

35 Above mentioned black powder is evacuated at 150°C for 1 hour, then 0.2 g of it is added as a catalyst into mixed solution of 0.1mol acetic acid and 1.0mol ethyl alcohol under argon gas flow, stirred at 70°C for 6 hours and the amount of ethyl acetate formed by acid catalyst reaction is detected by a gas chromatography. Results are shown in Fig. 13. Clearly understood from the Figure, forming speed of ethyl acetate is slow under the presence of synthesized catalyst, and is confirmed that acid catalytic function of the synthesized material is very small.

## 40 INDUSTRIAL APPLICABILITY

45 [0043] Solid strong acid or solid strong acid - carbon material composite of the present invention which are insoluble in a polar solvent is a material having strong acid characteristic produced by relatively easy method using cheap material, therefore, brings an excellent effect that are advantageous from view points of cost, function and industry.

## Claims

- 50 1. A method of condensing and sulphonating polycyclic aromatic hydrocarbons, comprising heat treating polycyclic aromatic hydrocarbons in concentrated sulphuric acid or fuming sulphuric acid at a temperature T of 200°C 450°C, to thereby prepare a solid acid which is insoluble in a polar solvent, wherein the polycyclic aromatic hydrocarbons are selected from naphthalene, anthracene, perylene, coronene and mixtures thereof, tar, pitch, fuel oil and asphalt containing a polycyclic aromatic hydrocarbon in which two or more aromatic rings are condensed.
- 55 2. A method according to claim 1, wherein the temperature T for heat treatment is  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$ .
3. A solid acid obtainable by a method according to either claim 1 or claim 2.

4. A method of condensation and sulfonation which method comprises heat treating a blend of polycyclic aromatic hydrocarbons and a carbon material in concentrated sulphuric acid or fuming sulphuric acid at a temperature of T of from  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$  to provide a composite solid strong acid which is insoluble in a polar solvent, wherein the polycyclic aromatic hydrocarbons are selected from naphthalene, anthracene, perylene, coronene and mixtures thereof, tar, pitch, fuel oil and asphalt containing a polycyclic aromatic hydrocarbon in which two or more aromatic rings are condensed, and wherein the carbon material is at least one selected from carbon black, acetylene black, activated carbon, carbon nano tube and fullerene.
5. A method according to claim 4, wherein the temperature T for heat treatment is  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$ .
6. A composite solid strong acid obtainable by a method according to either claim 4 or claim 5.

### Patentansprüche

1. Verfahren zur Kondensierung und Sulfonierung von polycyclischen aromatischen Kohlenwasserstoffen, umfassend das Wärmebehandeln von polycyclischen aromatischen Kohlenwasserstoffen in konzentrierter Schwefelsäure oder rauchender Schwefelsäure bei einer Temperatur T von  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$ , um dadurch eine Festkörpersäure herzustellen, die in einem polaren Lösungsmittel unlöslich ist, wobei die polycyclischen aromatischen Kohlenwasserstoffe ausgewählt sind aus Naphthalin, Anthracen, Perylen, Coronen, und Gemischen davon, Teer, Pech, Heizöl und Asphalt, enthaltend einen polycyclischen aromatischen Kohlenwasserstoff, in dem zwei oder mehrere aromatische Ringe kondensiert sind.
2. Verfahren nach Anspruch 1, wobei die Temperatur T zur Wärmebehandlung  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$  beträgt.
3. Festkörpersäure, die durch ein Verfahren entweder nach Anspruch 1 oder Anspruch 2 erhältlich ist.
4. Verfahren zur Kondensation und Sulfonierung, wobei das Verfahren das Wärmebehandeln einer Mischung von polycyclischen aromatischen Kohlenwasserstoffen und einem Kohlenstoffmaterial in konzentrierter Schwefelsäure oder rauchender Schwefelsäure bei einer Temperatur T von  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$  umfasst, um eine starke Festkörper-Verbundsäure herzustellen, die in einem polaren Lösungsmittel unlöslich ist, wobei die polycyclischen aromatischen Kohlenwasserstoffe ausgewählt sind aus Naphthalin, Anthracen, Perylen, Coronen und Gemischen davon, Teer, Pech, Heizöl und Asphalt, enthaltend einen polycyclischen aromatischen Kohlenwasserstoff, in dem zwei oder mehrere aromatische Ringe kondensiert sind, und wobei das Kohlenstoffmaterial mindestens eines ist, das ausgewählt ist aus Ruß, Acetylenruß, Aktivkohle, Kohlenstoff-Nanoröhrchen und Fulleren.
5. Verfahren nach Anspruch 4, wobei die Temperatur T zur Wärmebehandlung  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$  beträgt.
6. Starke Festkörper-Verbundsäure, die durch ein Verfahren entweder nach Anspruch 4 oder Anspruch 5 erhältlich ist.

### Revendications

1. Procédé de condensation et de sulfonation d'hydrocarbures aromatiques polycycliques, comprenant le traitement thermique d'hydrocarbures aromatiques polycycliques dans de l'acide sulfurique concentré ou de l'acide sulfurique fumant à une température T de  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$ , pour préparer ainsi un acide solide qui est insoluble dans un solvant polaire, dans lequel les hydrocarbures aromatiques polycycliques sont choisis parmi le naphthalène, l'anthracène, le pérylène, le coronène, et leurs mélanges, le goudron, le brai, le mazout et l'asphalte contenant un hydrocarbure aromatique polycyclique dans lequel deux cycles aromatiques ou plus sont condensés.
2. Procédé selon la revendication 1, dans lequel la température T pour le traitement thermique est de  $200^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$ .
3. Acide solide que l'on peut obtenir par un procédé selon la revendication 1 ou la revendication 2.
4. Procédé de condensation et de sulfonation, lequel procédé comprend le traitement thermique d'un mélange d'hydrocarbures aromatiques polycycliques et d'une matière carbonée dans de l'acide sulfurique concentré ou de l'acide sulfurique fumant à une température T de  $200^{\circ}\text{C} \leq T \leq 450^{\circ}\text{C}$  pour donner un acide fort solide composite qui est

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insoluble dans un solvant polaire, dans lequel les hydrocarbures aromatiques polycycliques sont choisis parmi le naphthalène, l'anthracène, le pérylène, le coronène, et leurs mélanges, le goudron, le brai, le mazout et l'asphalte contenant un hydrocarbure aromatique polycyclique dans lequel deux cycles aromatiques ou plus sont condensés, et dans lequel la matière carbonée est au moins l'un choisi parmi le noir de carbone, le noir d'acétylène, le charbon actif, un nanotube de carbone et le fullerène.

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5. Procédé selon la revendication 4, dans lequel la température T pour le traitement thermique est de  $200\text{ °C} \leq T \leq 350\text{ °C}$ .

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6. Acide fort solide composite pouvant être obtenu par un procédé selon la revendication 4 ou la revendication 5.

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Fig.1

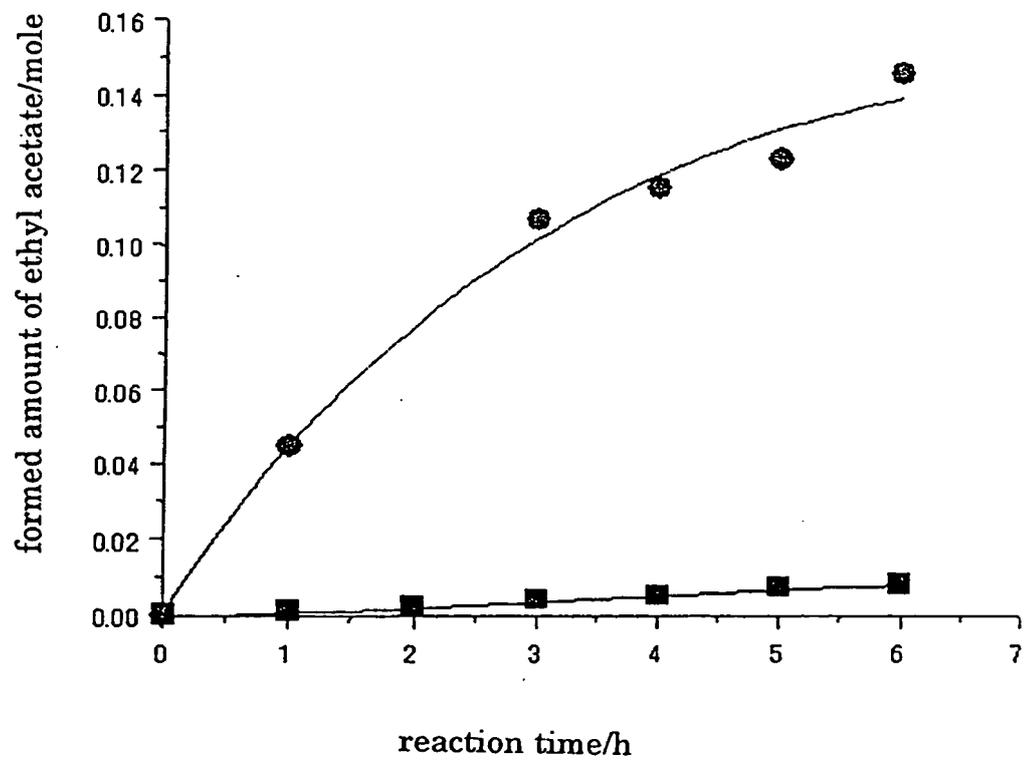


Fig.2

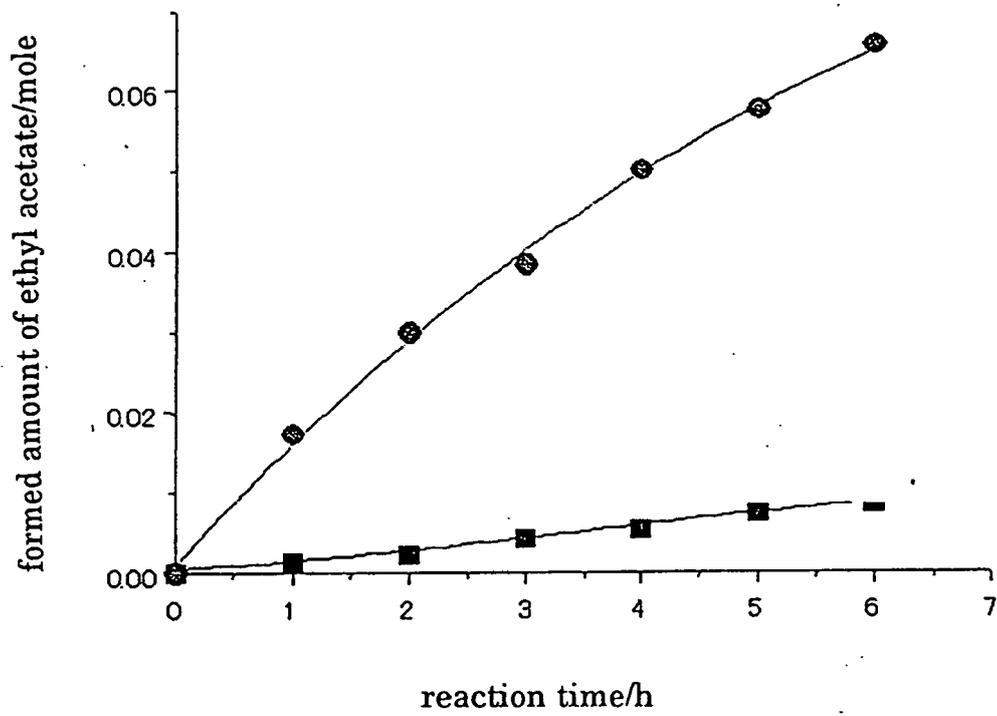


Fig.3

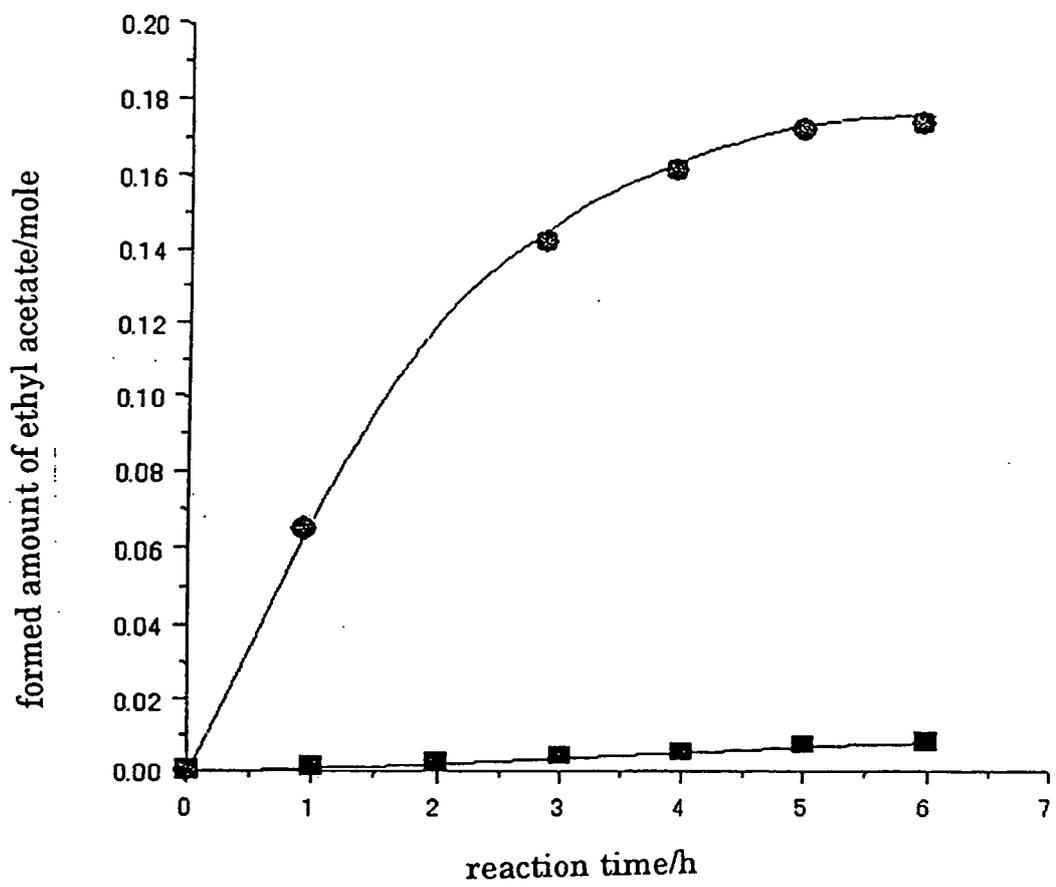


Fig.4

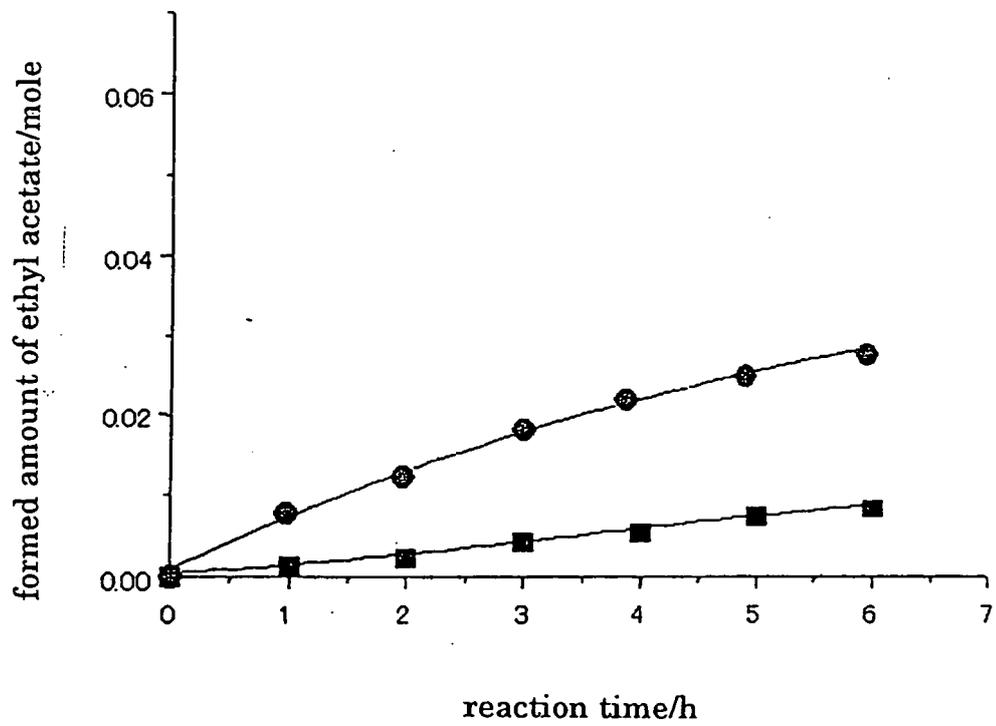


Fig.5

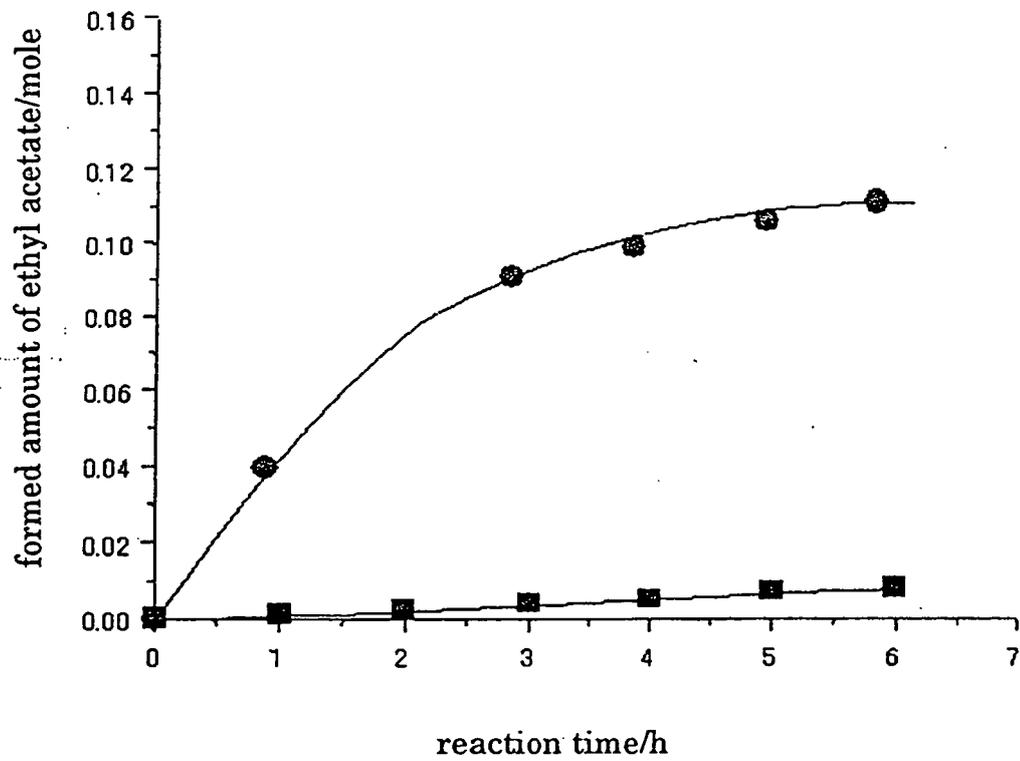


Fig.6

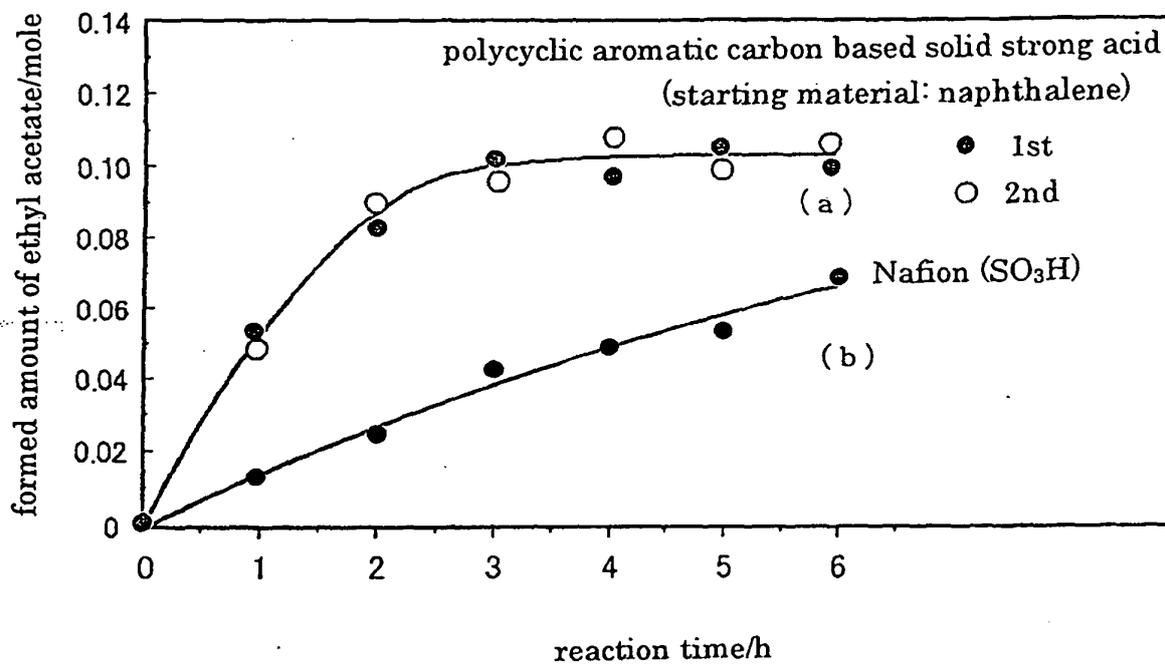


Fig.7

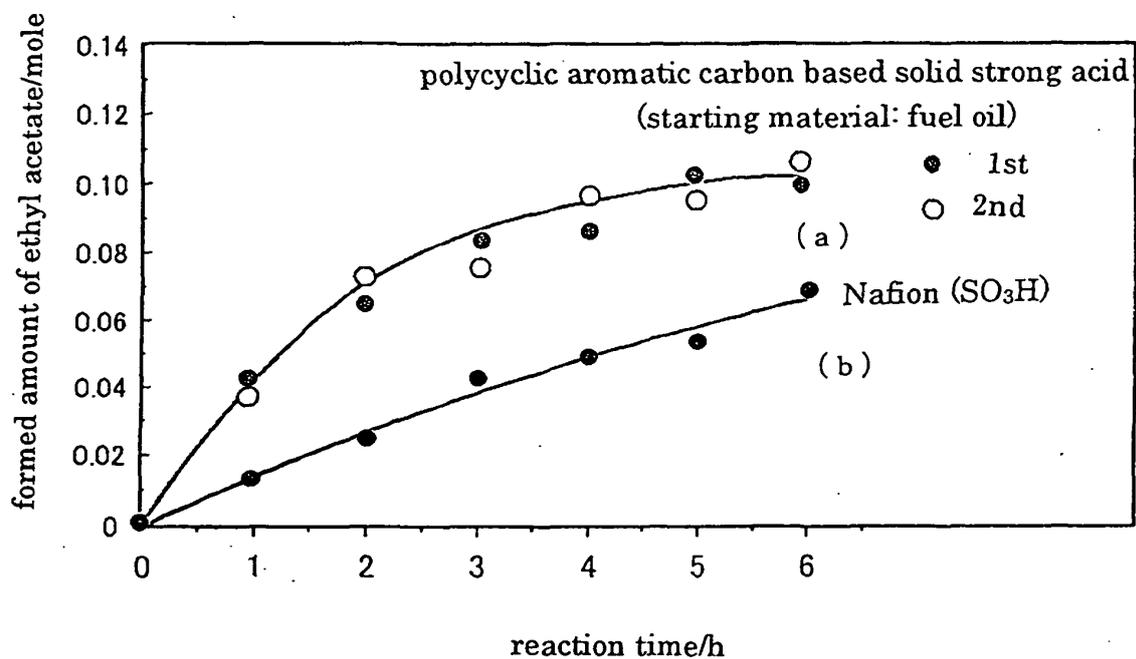


Fig.8

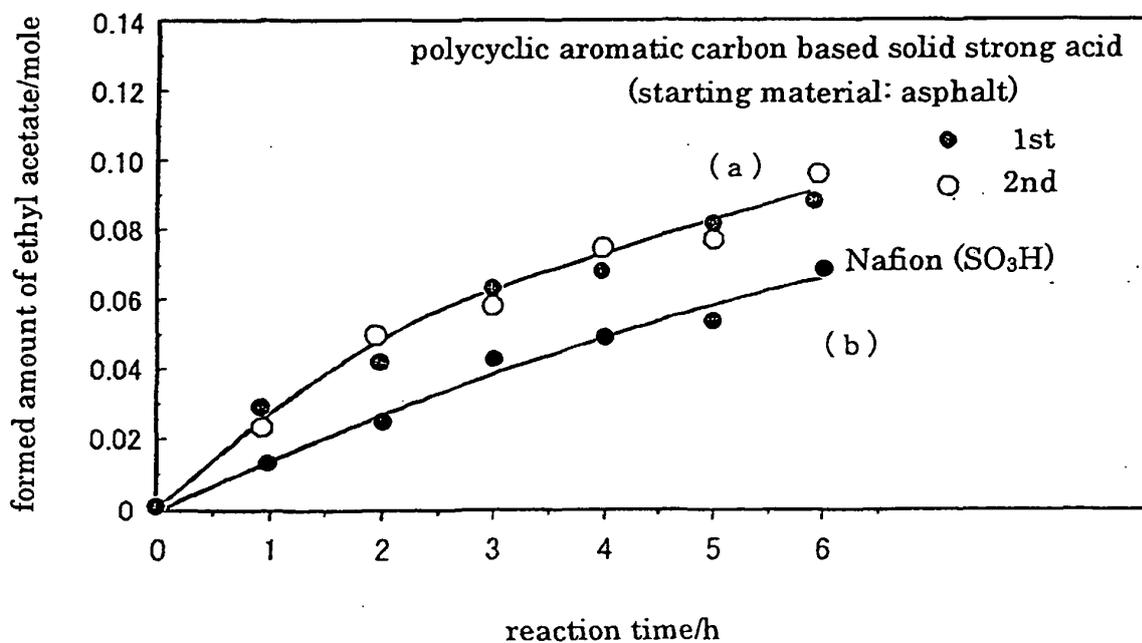


Fig.9

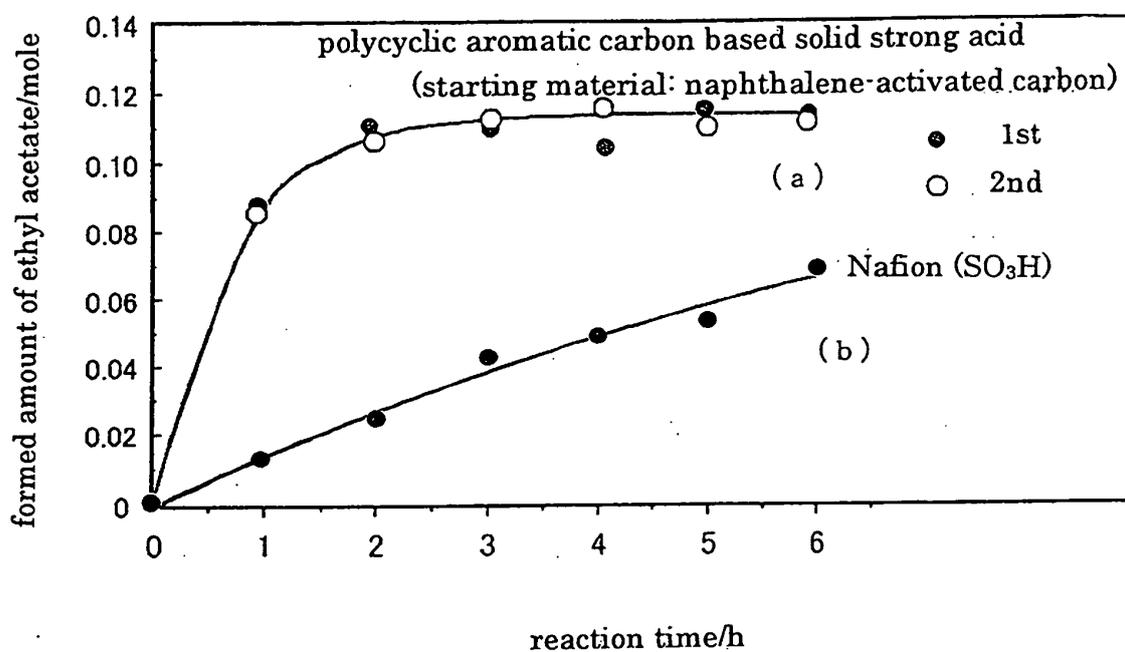


Fig.10

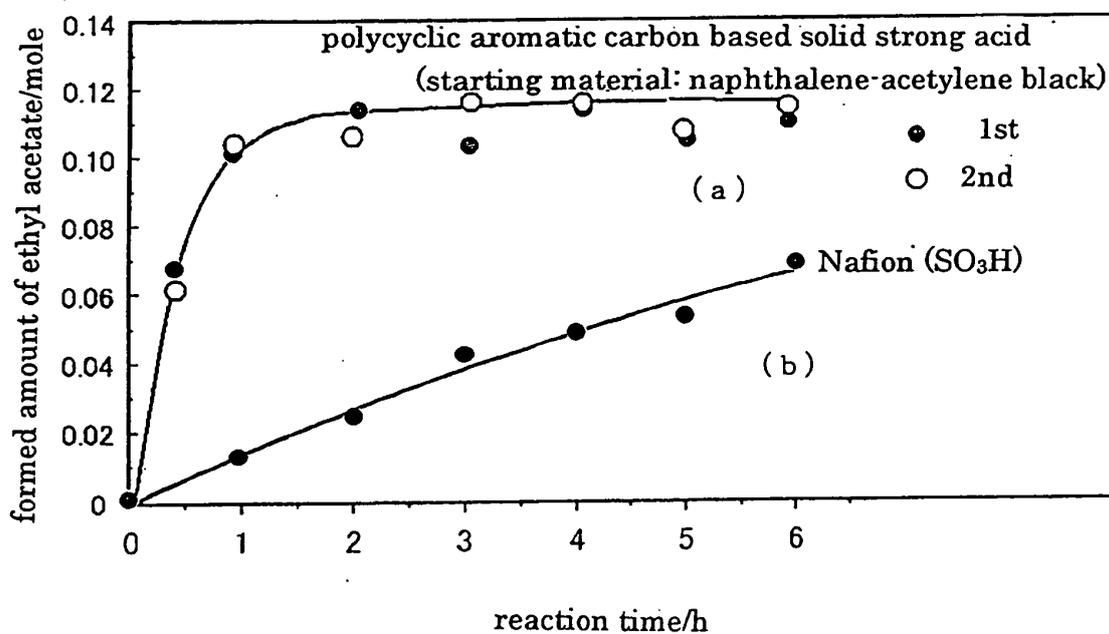


Fig.11

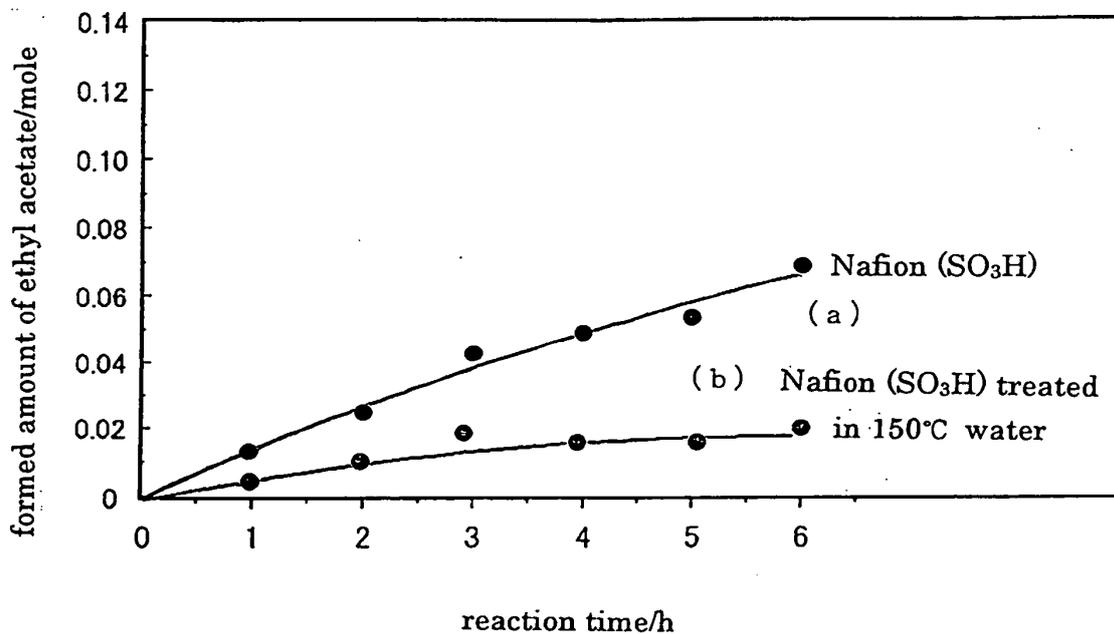


Fig.12

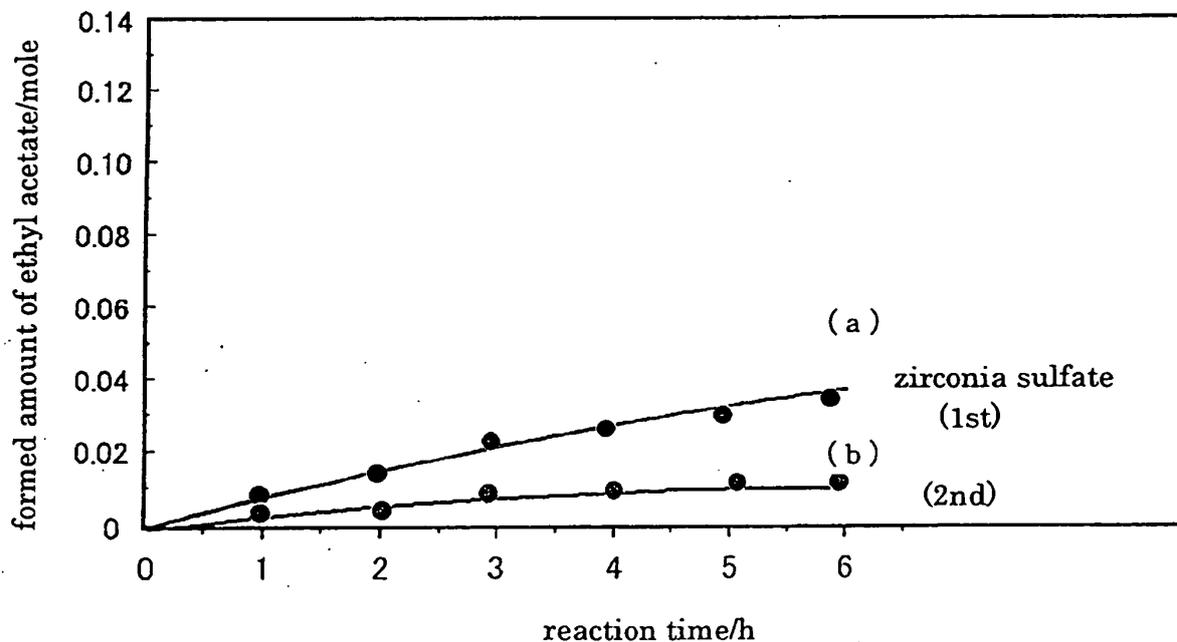
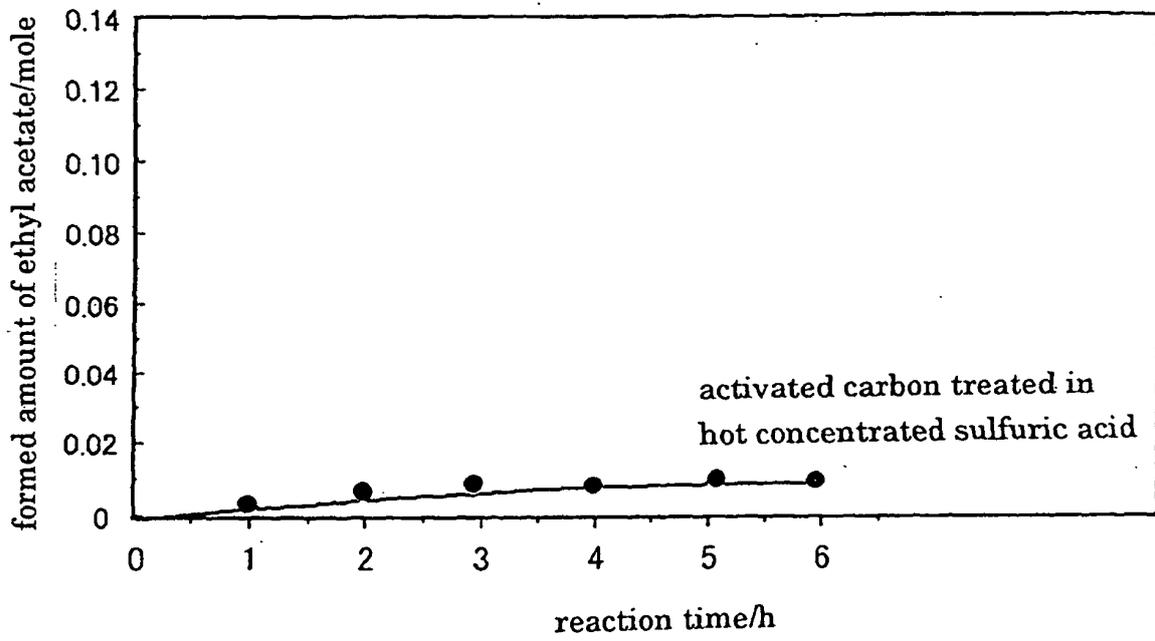


Fig.13



**REFERENCES CITED IN THE DESCRIPTION**

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**Non-patent literature cited in the description**

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