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(54) Benævnelse: **Katalysator til hydrolyse af carbonylsulfid og hydrogencyanid og anvendelse af titanoxid-baseret sammensætning**

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DESCRIPTION

[Technical Field]

[0001] The present invention relates to a catalyst for hydrolysis of carbonyl sulfide and hydrogen cyanide.

[Background Art]

[0002] Effective utilization of coal has attracted attention as a last resort to the recent energy issue. To convert coal to a high-value added energy medium, advanced technologies such as a technology for gasifying coal and a technology for purifying the gasified gas are employed.

[0003] The gasified coal gas contains carbonyl sulfide (COS) and hydrogen cyanide (HCN), which cause air pollution. Hence, it is important to remove these compounds in a gas purification step.

[0004] A purification process of gasified coal gas may be configured, for example, as shown in Fig. 1. Specifically, gas obtained by gasifying coal in a gasification furnace 4 and subjected to a dust removal treatment in a dust removal apparatus 5 is introduced into a COS conversion apparatus 6 to convert COS in the gas to carbon dioxide (CO_2) and hydrogen sulfide (H_2S), which are then recovered in an H_2S/CO_2 recovery apparatus 7. The thus purified gas is then used for synthesis 8 of chemicals, electric power generation 9, or the like.

[0005] Moreover, systems are also proposed in which the purified gas obtained by gasifying and purifying coal is applied to synthesis of chemicals such as methanol and ammonia or used directly for electric power generation. The electric power generation system includes the integrated coal gasification combined cycle (IGCC) system (for example, Patent Document 1). Specifically, in this system, coal is converted to a combustible gas in a high-temperature and high-pressure gasification furnace, and electric power is generated by a combination of a gas turbine and a steam turbine using the gasified gas as a fuel.

[0006] The COS conversion is based on the hydrolysis reaction represented by the following Formula (1), and an example of the catalyst for the hydrolysis is a catalyst obtained by supporting a metal carbonate on titanium dioxide (Patent Document 2).
[Math 1]

$$COS + H_2O \rightarrow CO_2 + H_2S \qquad (1)$$

[0007] Meanwhile, HCN can be converted to ammonia (NH_3) by the hydrolysis reaction of the following Formula (2) or the reaction of Formula (3), and the ammonia can be recovered. An example of the catalyst for hydrolysis of HCN is a titanium dioxide-based composition containing a combination of titanium dioxide, a sulfate of an alkaline-earth metal, and a doping compound (Patent Document 3).

[0008] Patent Document 4 discloses a catalyst for hydrolyzing carbonyl sulfide, the catalyst comprising either (a) a support made of TiO_2 and an active component selected from a metal sulfate and a metal carbonate supported thereon, or (b) a composite oxide selected from TiO_2/SiO_2, TiO_2/Al_2O_3, TiO_2/ZrO_2, Al_2O_3/SiO_2 and Al_2O_3/ZrO_2.

[0009] Patent Document 5 discloses a catalyst for hydrolyzing carbonyl sulfide, the catalyst comprising a support selected from Al_2O_3, Al_2O_3/TiO_2 and Al_2O_3/ZrO_2, and an active component supported thereon. The active component, in turn, includes a first component selected from at least one of Na_2CO_3 and K_2CO_3, and a second component selected from at least one oxide of Be, Mg, Ca, Sr, Ba, Zn, Fe, Co, Ni and Cu.
[Math 2]

$$HCN + H_2O \rightarrow NH_3 + CO \qquad (2)$$

$$HCN + 3H_2 \rightarrow NH_3 + CH_4 \qquad (3)$$

[Prior Art Documents]

[Patent Documents]

[0010]

[Patent Document 1] Japanese Patent Application Publication No. 2004-331701

[Patent Document 2] Japanese Patent No. 3746609

[Patent Document 3] Japanese Patent No. 4556159

[Patent Document 4] Japanese Patent Application Publication No. H11-276897

[Patent Document 5] Chinese Patent Application Publication No. 101239319

[Summary of Invention]

[Technical Problems]

[0011] Gasification and purification of coal requires many steps (Fig. 1). Hence, conducting each step in shorter period leads to shortening of the production period and reduction in costs.

[0012] For this reason, it can be said that, for example, providing a catalyst having better decomposition performance than hydrolysis catalysts used so far in the conversion step of COS and HCN is a novel object.

[Solution to Problems]

[0013] The present inventors have focused on the conversion step of COS and HCN, and reinvestigated the reaction mechanisms and reaction catalysts of the hydrolysis reactions of COS and HCN.

[0014] As a result, the present inventors have found that COS and HCN can be removed simultaneously at high degradation percentages when an active component containing a predetermined metal as a main component is supported on a titanium dioxide-based support having excellent corrosion resistance in a highly dispersed manner. This finding has led to the completion of the present invention. The invention is defined by the claims.

[0015] In a first aspect, the present invention thus relates to a catalyst as defined in claim 1. The catalyst comprises at least:

an active component containing barium carbonate; and

a titanium dioxide-based support supporting the active component, wherein the support comprises composite oxides of titanium dioxide and silicon dioxide, or composite oxides of titanium dioxide and aluminum oxide.

[0016] In a second aspect, the present invention relates to the use of the catalyst according to the first aspect for hydrolyzing carbonyl sulfide and hydrogen cyanide as defined in claim 3.

[Advantageous Effects of Invention]

[0017] The catalyst of the present invention makes it possible to remove COS and HCN simultaneously at high degradation percentages.

[Brief Description of Drawings]

[0018] [Fig. 1] Fig. 1 is a schematic diagram of an entire coal gasification and purification process.

[Description of Embodiment]

[0019] Hereinafter, a catalyst for hydrolysis of carbonyl sulfide and hydrogen cyanide and the use of this catalyst are described in detail.

[0020] First, the catalyst of the present invention is a catalyst for hydrolyzing carbonyl sulfide and hydrogen cyanide, and comprises at least an active component containing, as a main component, barium carbonate. The use of this metal salt makes it possible to achieve satisfactorily high decomposition performance of not only carbonyl sulfide but also hydrogen cyanide. The amount of the main component supported is preferably 0.1 to 25% by mass, and more preferably 5 to 22% by mass.

[0021] Moreover, the catalyst of the present invention comprises a titanium dioxide-based support supporting the active component. The titanium dioxide-based support is a composite oxide of titanium dioxide with either silicon dioxide or aluminum oxide.

[0022] Such a support can immobilize the active component reliably. In addition, the support is chemically stable under operating conditions of the catalyst, and hence does not inhibit the activity of the catalyst.

[0023] In the catalyst of the present invention, the titanium dioxide-based composition is preferably obtained by adding, to the titanium dioxide-based support, barium carbonate. This is because this material is stable as raw material.

[0024] In the catalyst of the present invention, a titanium dioxide-based composite oxide is used as the titanium dioxide-based support.

[0025] When titanium dioxide is converted to a composite metal oxide, the specific surface area increases, and the heat resistance also improves.

[0026] The titanium dioxide-based composite oxide is either a composite oxide of titanium dioxide and silicon dioxide, or a composite oxide of titanium dioxide and aluminum oxide. The composite ratio of titanium dioxide to the metal oxide composited with the titanium dioxide is preferably 1:99 to 99:1, and particularly preferably in a range from 50:50 to 95:5. This is because the specific surface area on which the active component is supported can be large in this range.

[0027] In the catalyst of the present invention, the titanium dioxide-based composition preferably has a honeycomb shape. This is because clogging and pressure drop of the catalyst and the titanium dioxide-based composition can be prevented even in a situation in which dust or the like is coexistent, so that the catalyst can be maintained in a highly active state.

[0028] In the catalyst of the present invention, the titanium dioxide-based composition can be produced, for example, as follows. Specifically, the above-described metal salt is added to a powder of the titanium dioxide-based support, and further a binder and a plasticizer are added. Then, the mixture is kneaded, molded into a spherical shape, a pellet shape, or a honeycomb shape, as appropriate, and then dried and calcined.

[0029] In addition, since the support is made of a titanium dioxide-based composite oxide, it is necessary to prepare the composite oxide in advance. The composite oxide can be prepared, for example, as follows. Specifically, coprecipitation is conducted by adding dropwise an alkali solution of ammonia or the like to an aqueous solution of metal salts such as nitrates, chlorides, and sulfates of titanium, silicon and aluminum. Thus, a composite hydroxide is formed. Then, the composite hydroxide is, for example, rinsed, dried, and calcined. The composite oxide can also be prepared by methods other than this method.

[Examples]

[0030] Hereinafter, the present invention is described more specifically based on Examples and Comparative Example. However, the present invention is not at all limited to the following Examples.

[Production of Catalysts for Hydrolysis]

[Example 1] (not according to the invention)

[0031] To 100 parts by mass of an anatase-type titanium dioxide powder (CSP-003 manufactured by JGC Catalysts and Chemicals Ltd.), 4 parts by mass, in terms of barium oxide, of barium carbonate (manufactured by HAYASHI PURE CHEMICAL IND., LTD., special grade reagent) was added, and 5 parts by mass of 10% ammonia water was added, followed by kneading with a kneader for 60 minutes. Next, to the kneaded material, 3 parts by mass of glass fiber and 5 parts by mass of kaolin as binders, 5 parts by mass of cellulose acetate as an organic plasticizer, and 5 parts by mass of 10% ammonia water were added, followed by kneading.

[0032] The kneaded material was extrusion molded to obtain a monolithic honeycomb molded article having a pitch of 5.0 mm and a wall thickness of 1.0 mm. The molded article was dried at room temperature until the water content reached 10%, and then calcined at 500°C for 5 hours to remove the organic plasticizer. Thus, a honeycomb catalyst was obtained.

[Example 2] (not according to the invention)

[0033] A honeycomb catalyst was obtained in the same method as in Example 1, except that 4 parts by mass, in terms of nickel oxide, of nickel carbonate (manufactured by HAYASHI PURE CHEMICAL IND., LTD., special grade reagent) was added instead of barium carbonate.

[Example 3] (not according to the invention)

[0034] A honeycomb catalyst was obtained in the same method as in Example 1, except that 0.1 parts by mass, in terms of ruthenium, of ruthenium nitrate (manufactured by Tanaka Kikinzoku Kogyo K. K., Ru content: 50 g/L) was added instead of barium carbonate.

[Example 4] (not according to the invention)

[0035] A honeycomb catalyst was obtained in the same method as in Example 1, except that 4 parts by mass, in terms of nickel oxide, of nickel carbonate and 10 parts by mass, in terms of molybdenum oxide, of ammonium molybdate (manufactured by HAYASHI PURE CHEMICAL IND., LTD., special grade) were added instead of barium carbonate.

[Example 5] (not according to the invention)

[0036] A honeycomb catalyst was obtained in the same method as in Example 1, except that 5 parts by mass, in terms of cobalt oxide, of cobalt carbonate (manufactured by HAYASHI PURE CHEMICAL IND., LTD., special grade) and 10 parts by mass, in terms of molybdenum oxide, of ammonium molybdate were added instead of barium carbonate.

[Example 6]

[0037] A honeycomb catalyst was obtained in the same method as in Example 1, except that a composite oxide of titanium dioxide and silicon dioxide obtained as follows was used as the support. Specifically, 1125.8 g of $Ti(Oi\text{-}C_3H_7)_4$ as a Ti source and 57.6 g of $Si(OC_2H_5)_4$ were mixed with each other. The mixture was hydrolyzed by being added to 15000 g of water at

80°C, and further aged by being stirred in water at the same temperature for 2 hours. After the aging, the obtained product was filtered and washed sufficiently. Then, the product was dried and calcined (at 500°C for 5 hours). Thus, the composite oxide of titanium dioxide and silicon dioxide was obtained.

[Example 7]

[0038] A honeycomb catalyst was obtained in the same method as in Example 6, except that a composite oxide of titanium dioxide and aluminum oxide obtained by using 316.8 g of $Al(Oi\text{-}C_3H_7)_3$ instead of $Si(OC_2H_5)_4$ used in Example 6 was used as the support.

[Example 8] (not according to the invention)

[0039] A honeycomb catalyst was obtained in the same method as in Example 6, except that a composite oxide of titanium dioxide and zirconium dioxide obtained by using 985.5 g of $Zr(O\text{-}iC_4H_9)_4$ instead of $Si(OC_2H_5)_4$ used in Example 6 was used as the support.

[Comparative Example 1]

[0040] To 100 parts by mass of an anatase-type titanium dioxide powder (CSP-003 manufactured by JGC Catalysts and Chemicals Ltd.), 5 parts by mass of 10% ammonia water was added, followed by kneading with a kneader for 60 minutes. Next, to the kneaded material, 3 parts by mass of glass fiber and 5 parts by mass of kaolin as binders, 5 parts by mass of cellulose acetate as an organic plasticizer, and 5 parts by mass of 10% ammonia water were added, followed by kneading.

[0041] The kneaded material was extrusion molded to obtain a monolithic honeycomb molded article having a pitch of 5.0 mm and a wall thickness of 1.0 mm. This molded article was dried at room temperature until the water content reached 10%, and it was then calcined at 500°C for 5 hours to remove the organic plasticizer. Thus, a honeycomb catalyst was obtained.

[Hydrolysis Reaction of COS]

[0042] Hydrolysis reaction of COS was conducted by using the catalysts of Examples and Comparative Example described above under the test conditions shown in Table 1. The COS conversion was calculated by the following Formula (4). Table 2 shows the results.

[0043] [Math 3]

$$\text{COS conversion (\%)} = (1 - \text{Outlet COS concentration}/\text{Inlet COS concentration}) \times 100 \qquad (4)$$

[Table 1]

Catalyst amount: 10cc	(Gas composition)
Gas flow rate: 60literN/h	H_2: 10%
GHSV: 6000h^{-1}	CO: 25%
Pressure: 9kgf/cm^2	H_2O: 3.2%
Temperature: 300°C	CO_2: 3.5%
	COS: 210ppm
	H_2S: 880ppm
	N_2: the balance

[Table 2]

	Catalyst composition	COS conversion (%)
Example 1*	$BaCO_3/TiO_2$	79
Example 2*	$NiCO_3/TiO_2$	78
Example 3*	$Ru(NO_3)_3/TiO_2$	76
Example 4*	$NiCO_3+(NH_4)_6Mo_7O_{24} \bullet 4H_2O/TiO_2$	80
Example 5*	$CoCO_3+(NH_4)_6Mo_7O_{24} \bullet 4H_2O/TiO_2$	78
Example 6	$BaCO_3/TiO_2SiO_2$	83
Example 7	$BaCO_3/TiO_2Al_2O_3$	80
Example 8*	$BaCO_3/TiO_2ZrO_2$	79
Comparative Example 1	TiO_2	47

* (not according to the invention)

[0044] The results in Table 2 showed that each of the catalysts of the Examples was better in COS conversion performance than the catalyst of Comparative Example 1.

[Hydrolysis Reaction of HCN]

[0045] Hydrolysis reaction of HCN was conducted by using the catalysts of Examples and Comparative Example described above and actual gasified coal gas shown in Table 3. The HCN conversion was calculated by the following Formula (5). Table 4 shows the results.

[0046] [Math 4]

$$\text{HCN conversion (\%)} = (1\text{-Outlet HCN concentration/Inlet HCN concentration}) \times 100 \qquad (5)$$

[Table 3]

	(Gas composition)
Catalyst amount: 10 liter	Gasified gas composition
Gas flow rate: $60m^3N/h$	H_2: 10%
GHSV: $6000h^{-1}$	CO: 25%
Pressure: $9kgf/cm^2$	H_2O: 3.2%
Temperature: 300-350 °C	CO_2: 3.5%
	COS: 210ppm
	H_2S: 880ppm
	HCN : 1-70ppm
	N_2: balance

[Table 4]

	Catalyst composition	HCN conversion (%)
Example 1*	$BaCO_3/TiO_2$	100
Example 2*	$NiCO_3/TiO_2$	99
Example 3*	$Ru(NO_3)_3/TiO_2$	99
Example 4*	$NiCO_3+(NH_4)_6Mo_7O_{24} \bullet 4H_2O/TiO_2$	100
Example 5*	$CoCO_3+(NH_4)_6Mo_7O_{24} \bullet 4H_2O/TiO_2$	99
Example 6	$BaCO_3/TiO_2SiO_2$	100
Example 7	$BaCO_3/TiO_2Al_2O_3$	99
Example 8*	$BaCO_3/TiO_2ZrO_2$	100
Comparative Example 1	TiO_2	50
* (not according to the invention)		

[0047] The results in Table 4 showed that each of the catalysts of Examples was better in HCN decomposition performance than the catalyst of Comparative Example 1.

[0048] From these results, it is apparent that the catalyst of the present invention is excellent in COS conversion performance and HCN decomposition performance.

[Industrial Applicability]

[0049] The catalyst for hydrolysis of carbonyl sulfide and hydrogen cyanide is industrially useful, because COS and HCN can be removed simultaneously at high degradation percentages.

[Reference Signs List]

[0050]

1	coal gasification and purification process
2	coal
3	oxygen
4	gasification furnace
5	dust removal apparatus
6	COS conversion apparatus
7	H_2S/CO_2 recovery apparatus
8	synthesis of chemicals
9	electric power generation

REFERENCES CITED IN THE DESCRIPTION

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Patentkrav

1. En katalysator, omfattende mindst:

en aktiv komponent indeholdende bariumcarbonat; og
en titandioxid-baseret support, der støtter den aktive komponent,
hvor supporten omfatter kompositoxider af titandioxid og siliciumdioxid, eller kompositoxider af titandioxid og aluminiumoxid.

2. Katalysatoren ifølge krav 1, hvor katalysatoren har en honeycomb-form.

3. Anvendelse af katalysatoren ifølge krav 1 eller 2 til at hydrolysere carbonylsulfid og hydrogencyanid.

DRAWINGS

FIG.1