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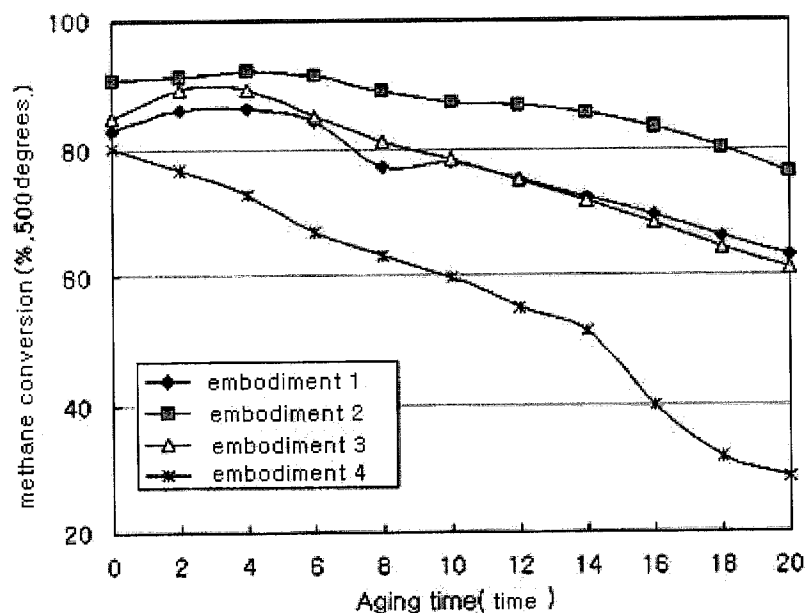
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(54) Title: A CATALYST FOR TREATING EXHAUST GAS OF DIESEL LNG DUAL FUEL VEHICLES

[Figure 2]



(57) Abstract: The present invention relates to a catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, in which palladium and platinum as catalyst active ingredients are impregnated. The catalyst for treating exhaust gas of diesel LNG dual fuel vehicles has the excellent methane oxidation activity and the excellent sulfur poisoning prevention effect.

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【DESCRIPTION】**【Invention Title】**

A CATALYST FOR TREATING EXHAUST GAS OF DIESEL LNG DUAL FUEL VEHICLES

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【Technical Field】

The present invention relates to a catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, and more particularly, to a catalyst of diesel LNG dual fuel vehicles, which can efficiently remove methane contained in the exhaust gas of diesel LNG dual fuel vehicles and also has excellent resistance to sulfur poisoning.

【Background Art】

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A natural gas vehicle can be classified into a CNG type and an LNG type according to a fuel supply system. The CNG type uses gas compressed at a pressure of about 200 atmospheres and stored in a high-pressure vessel, and the LNG type uses cryogenic fuel having a temperature of approximately -130°C. It seems that the reason why CNG is mainly used as the natural gas fuel at home and abroad is that it is difficult to apply LNG to vehicles compared with CNG and there is insufficient infrastructure for supplying LNG. In case of Korea, the CNG vehicle is well received in the market and is

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in a matured stage, but the LNG vehicle is just passed a developing stage and now in a test driving stage.

Meanwhile, a natural gas engine can be classified into a dedicated type and a dual fuel type according to an ignition system. The dedicated type employs an electrical ignition system and is mainly used in a gasoline engine, and the dual fuel type uses diesel fuel as an ignition source. In case that an existing gasoline vehicle is remodeled into the natural gas vehicle, if the dual fuel type is applied, it can achieve fuel conversion comparatively simply by installing only a natural gas supply system without changing an ignition system.

In the natural gas vehicle, methane is a main ingredient in the exhaust gas. The methane is a potential greenhouse gas having a long life span and shows a higher greenhouse effect than carbon dioxide. Due to environmental impact of the methane exhausted from the natural gas vehicle, it is expected that the emission regulation will be proposed sooner or later, and about 60% of the methane which is exhausted in the existing state of the natural gas vehicle should be treated by a low temperature post-treating apparatus and the like in order to conform with the strongest European regulation.

Recently, a catalyst in which palladium is impregnated as an active ingredient is used to oxidize the methane. However, there is a problem that palladium has a remarkably lowered

catalytic activity under sulfur conditions.

Meanwhile, in case of a diesel LNG dual fuel vehicle, since LNG does not contains sulfur but diesel contains sulfur, the catalytic active material for oxidizing the methane in the exhaust gas is poisoned by sulfur contained in diesel, and thus it is necessary to develop a methane removing catalyst for the diesel LNG dual fuel vehicle.

【Disclosure】

10 【Technical Problem】

An object of the present invention is to provide a catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, which can efficiently remove methane contained in the exhaust gas of the diesel LNG dual fuel vehicles.

15 Another object of the present invention is to provide a catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, which has high methane removing performance and excellent resistance to sulfur poisoning.

20 【Technical Solution】

From a result of repeated studies to achieve the above objects, the inventors had found that the sulfur poisoning phenomenon can be controlled by impregnating platinum as well as palladium in a catalyst while a weight ratio of platinum

and palladium is adjusted.

Generally, the diesel fuel is controlled to contain sulfur of 50ppm or less in Korea. Therefore, a sulfur concentration in the exhaust gas of the diesel LNG dual fuel vehicle is in an extent of 10ppm or less, 0.1 ~ 10ppm, more detailedly, 0.1 ~ 5ppm, although it depends on a mixed fuel burning ratio. In the present invention, a impregnating ratio of palladium and platinum had been adjusted to have excellent methane oxidation activity in the exhaust gas condition of the diesel LNG dual fuel vehicle. As a result, the inventors had found that, when the weight ratio of palladium and platinum is 1:0.1 ~ 0.5, it has high methane oxidation activity and excellent resistance to sulfur poisoning .

The present invention relates to a catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, in which palladium and platinum as catalyst active ingredients are impregnated in the weight ratio of 1:0.1 ~ 0.5, and more preferably, the catalyst for treating exhaust gas of diesel LNG dual fuel vehicles has a ceramic substrate on which a support that is treated by acidification, and palladium and platinum, as catalyst active ingredients, having the weight ratio of 1:0.1 ~ 0.5 are deposited.

Preferably, the weight ratio of palladium and platinum is 1:0.1 ~ 0.5, more preferably, 1:0.1 ~ 0.3.

The palladium has more excellent catalytic activity than the platinum, but it is easily poisoned by sulfur, so that the catalytic activity is deteriorated. Therefore, besides palladium, it is necessary to provide a cocatalyst for the sulfur poisoning prevention effect. The platinum has excellent effect as the cocatalyst having the sulfur poisoning prevention effect while maintaining the methane oxidation activity, but it has lower methane oxidation activity compared with the palladium. Thus, the ratio of platinum and palladium is important to provide the sulfur poisoning prevention effect and the excellent methane oxidation activity. Further, from the result of repeated studies, the inventors had found that, when the weight ratio of palladium and platinum is 1:0.1 ~ 0.5, more preferably, 1:0.1 ~ 0.3, it has the sulfur poisoning prevention effect and the excellent methane oxidation activity. If the weight ratio of the platinum with respect to the palladium is less than 0.1, the sulfur poisoning prevention effect is remarkably deteriorated, and if the weight ratio of the platinum with respect to the palladium is larger than 0.5, the methane oxidation activity is lowered. Therefore, only when the weight ratio of palladium and platinum is controlled within the above-mentioned extent, it can have the sulfur poisoning prevention effect and the excellent methane oxidation activity in the diesel LNG dual fuel vehicles.

The catalyst for treating exhaust gas of diesel LNG dual fuel vehicles according to the present invention has a ceramic substrate on which the support, and palladium and platinum as catalyst active ingredients are deposited. The ceramic
5 substrate may have a honeycomb monolith structure formed of a heat-resistant ceramic material like cordierite. The support may include alumina, zirconia, silica, ceria and a mixture thereof, but the alumina is more preferable in the aspect of catalytic activity. The support may be treated with acid like
10 sulfuric acid.

Preferably, an amount of the support washcoated on the ceramic substrate is $0.5 \sim 4\text{g/in}^3$. If the amount of the support is less than 0.5g/in^3 , catalyst performance is significantly deteriorated, and if the amount of the support
15 is larger than 4g/in^3 , the catalyst performance is enhanced any more and also it is not facile to manufacture it.

Further, in the present invention, a content of the catalytic active material impregnated in the catalyst is in an extent of $0.1 \sim 20$ weight%, preferably, $1 \sim 15$ weight% with
20 respect to total weight of the support and the catalytic active material. If the content is less than 0.1 weight%, catalyst performance is significantly deteriorated, and if the content is larger than 20 weight%, the catalyst performance is enhanced any more and it is disadvantage in the economical

point of view.

According to the present invention, after the support is wash-coated on the substrate, the catalytic active material may be impregnated in the wash-coated substrate. Alternatively, 5 after the catalytic active material is impregnated in the support, the support impregnating the catalytic active material may be wash-coated on the substrate.

The catalyst for treating exhaust gas of diesel LNG dual fuel vehicles can be manufactured by a method comprising the 10 steps of:

preparing a wash-coated substrate by wash-coating alumina on a ceramic substrate and then drying and calcining the wash-coated ceramic substrate; and

impregnating catalyst active ingredients by immersing the 15 wash-coated substrate in a catalytic solution containing palladium and platinum and then drying and calcining the wash-coated ceramic substrate.

The palladium precursor used for preparing the catalytic solution includes palladium nitrate, palladium chloride, 20 tetraamminepalladium chloride, and the like. The platinum precursor includes tetraammineplatinum nitrate($\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$) and hexachloroplatinic acid(H_2PtCl_6) and the like, but H_2PtCl_6 is further advantage in the point of the catalytic activity compared with $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$.

The wash-coating of the support on the substrate, and the drying and calcining can be performed by typical methods in the art.

5 **【Advantageous Effects】**

The catalyst for treating exhaust gas of diesel LNG dual fuel vehicles according to the present invention has the excellent methane oxidation activity and the excellent resistance to sulfur poisoning.

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【Description of Drawings】

The above and other objects, features and advantages of the present invention will become apparent from the following description of preferred embodiments given in conjunction with the accompanying drawings, in which:

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Fig. 1 is a graph showing an evaluation result of activity of a methane oxidation catalyst impregnating palladium and platinum as catalyst active ingredients.

Fig. 2 is a graph showing an evaluation result of resistance of the catalyst with respect to sulfur.

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【Best Mode】

Hereinafter, the embodiments of the present invention will be described in detail with reference to accompanying

drawings.

[Embodiments 1 to 7] Manufacturing of catalyst
impregnating Pd and Pt

Gamma alumina powder (SASOL, German, surface area:
5 $210\text{m}^2/\text{gr}$, pore volume: $0.5\text{cc}/\text{gr}$, specific gravity: $0.8\text{g}/\text{cc}$) is
mixed with a mixed solution of acetic acid and distilled water
(weight ratio of 1:3.5), and then uniform alumina slurry is
prepared by grinding it using a wet ball mill for 12hours. A
content of the gamma alumina powder in the slurry is 50
10 weight%, and an average particle size of the ground gamma
alumina powder is $3\mu\text{m}$.

Cordierite honeycomb monolith (1in^3 , 400 cpsi) is wash-
coated with the alumina slurry so that an amount of the
alumina washcoated is $2\text{g}/\text{in}^3$, dried for 2 hours at a
15 temperature of 120°C and then calcined for three hours at a
temperature of 550°C , thereby manufacturing the honeycomb
monolith washcoated with alumina.

Catalytic solutions of 80g are respectively prepared by
dissolving $\text{Pd}(\text{NO}_3)_2$ aqueous solution (10 weight%) as the
20 palladium precursor and H_2PtCl_6 as the platinum precursor in
distilled water so as to have each content as indicated in
Table 1. And, the honeycomb monolith washcoated with alumina
is immersed in each catalytic solution for 1 minute and then
treated by air-blowing so as to remove residual solution. Then,

the honeycomb monolith is dried for 2 hours at a temperature of 120°C under atmospheric pressure and then calcined for four hours at a temperature of 600°C, thereby manufacturing a catalyst impregnating palladium (Pd) and platinum (Pt).

5 [Embodiment 8]

A catalyst is manufactured in the same way as the embodiment 7 except that $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ is used as the platinum precursor.

Table 1

	Content of catalytic ingredient in catalytic solution (weight%) ^a		Pd:Pt (weight ratio)	Remark
	Pd	Pt		
Embodiment 1	0.5	1	1:2	
Embodiment 2	0.75	0.75	1:1	
Embodiment 3	1	0.5	1:0.5	
Embodiment 4	1.25	0.25	1:0.2	
Embodiment 5	4	2	1:0.5	4times impregnating amount
Embodiment 6	5	1	1:0.2	4times impregnating amount
Embodiment 7	2.5	0.5	1:0.2	2times impregnating amount
Embodiment 8	2.5	0.5	1:0.2	2times impregnating amount using $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$

10 a: A content of a catalytic ingredient in a catalytic solution

[Test example 1] Evaluation of catalytic activity

The honeycomb monolith catalysts manufactured in the embodiments 1 to 4 are fixed in a catalyst reactor, and then a methane (CH_4) oxidation experiment is performed.

5 Model gases having compositions as indicated in Table 2 are mixed in a controlled flow rate using MFC (mass flow controller) and then injected into the catalyst reactor. The flow rate of the model gases is 13.6 l/min and a space velocity is GHSV $50,000\text{hr}^{-1}$. A thermocouple is provided at
10 internal upper and lower sides of the catalyst reactor so as to control and measure a temperature, and a reaction temperature is in an extent of $150 \sim 600^\circ\text{C}$, and a temperature is increased in stages at a heating rate of $5^\circ\text{C}/\text{min}$, and then the catalytic activity is checked. Each concentration of NO,
15 CO , CH_4 reaction gases after/before the reaction is detected through a gas analyzer.

Table 2

Ingredient	Concentration
N_2	Balanced
Air	10%
NO	500ppm
CO	150ppm
CH_4	400ppm

Fig. 1 is a graph showing an evaluation result of activity of a methane oxidation catalyst impregnating
20 palladium and platinum as catalyst active ingredients. Referring to the result of Fig. 1, the catalyst in the

embodiment 4 in which a weight ratio of palladium and platinum is 1:0.2 has the most excellent catalytic activity.

[Test example 2] Evaluation of sulfur resistance

5 While model gases indicated in Table 3 are injected to the catalysts of embodiments 5 to 8, methane conversion at 500°C is evaluated by times. And the result is illustrated in Fig. 2.

Table 3

GHSV=100,000hr ⁻¹					
Reaction gas	10%NO/N ₂	700ppm SO ₂ / N ₂	10% CH ₄ /N ₂	Air	N ₂
Flow rate (ml/min)	45.54	19.37	36.43	9.42	17.62
Base concentration	500ppm (NOx)	1ppm	405ppm		

10 Referring to the result of Fig. 2, in the condition of Pd:Pt=1:0.2 (weight ratio) compared with Pd:Pt=1:0.5 (weight ratio), the methane conversion is further high, and the methane conversion becomes higher as the impregnating amount is increased. In the point of catalytic activity according to
15 the platinum precursor, H₂PtCl₆ has further excellent property compared with Pt(NH₃)₄(NO₃)₂.

Those skilled in the art will appreciate that the conceptions and specific embodiments disclosed in the
20 foregoing description may be readily utilized as a basis for modifying or designing other embodiments for

impregnating out the same purposes of the present invention. Those skilled in the art will also appreciate that such equivalent embodiments do not depart from the spirit and scope of the invention as set forth in the appended claims.

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【Industrial Applicability】

The catalyst for treating exhaust gas of diesel LNG dual fuel vehicles according to the present invention has the excellent methane oxidation activity and the excellent
10 resistance to sulfur poisoning.

【CLAIMS】**【Claim 1】**

A catalyst for treating exhaust gas of diesel LNG dual fuel vehicles, wherein palladium and platinum as catalyst
5 active ingredients are impregnated in the weight ratio of 1:0.1 ~ 0.5.

【Claim 2】

The catalyst according to claim 1, wherein the weight ratio of palladium and platinum is 1:0.1 ~ 0.3.

10 **【Claim 3】**

The catalyst according to claim 2, wherein the catalyst has a ceramic substrate on which a support selected from alumina, zirconia, silica, ceria and a mixture thereof, and palladium and platinum as catalyst active ingredients are
15 deposited.

【Claim 4】

The catalyst according to claim 3, wherein the support is alumina.

【Claim 5】

20 The catalyst according to claim 4, wherein the catalyst for treating exhaust gas of diesel LNG dual fuel vehicles can be manufactured by a method comprising the steps of:

preparing a wash-coated substrate by wash-coating alumina

on a ceramic substrate and then drying and calcining the wash-coated ceramic substrate; and

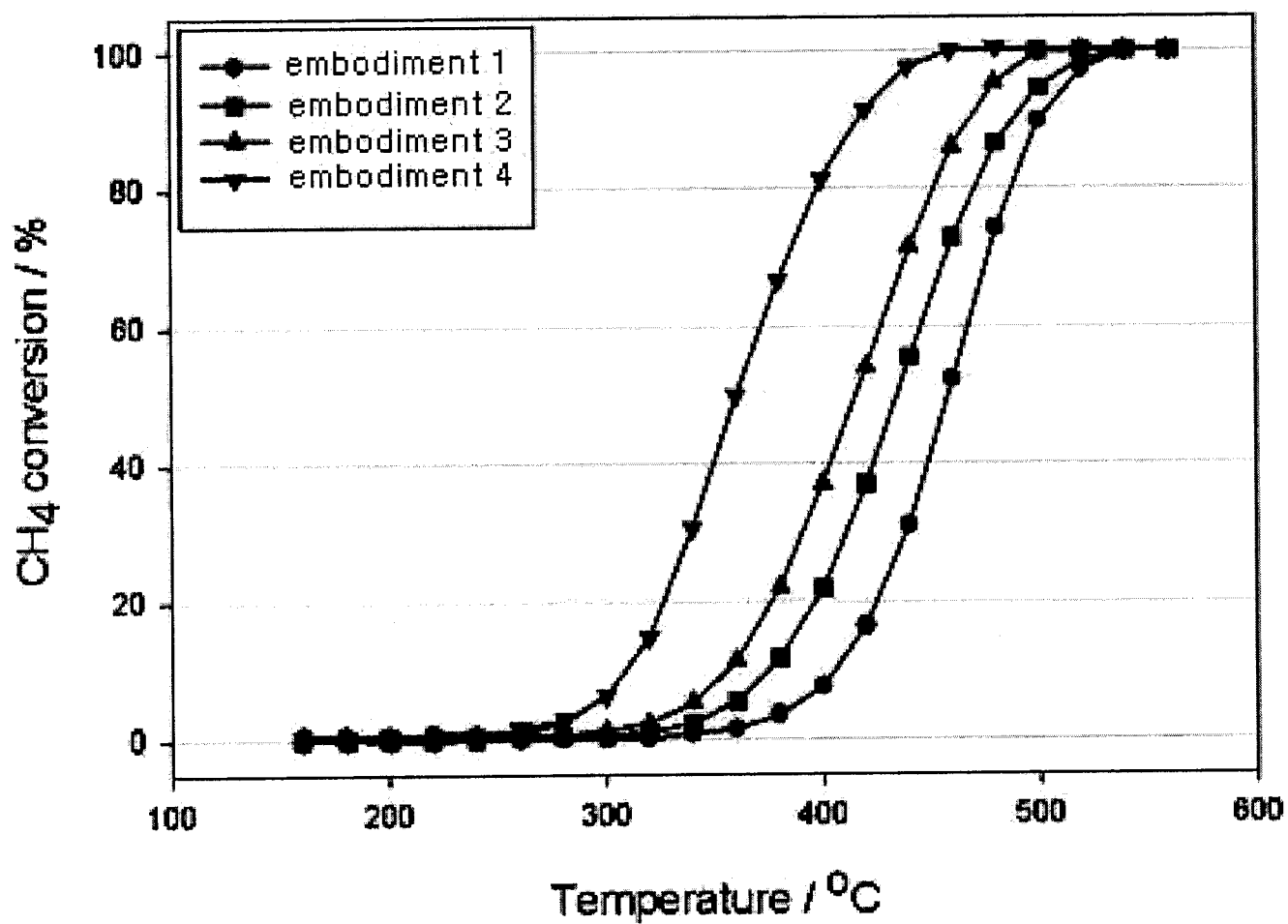
impregnating catalyst active ingredients by immersing the wash-coated substrate in a catalytic solution containing
5 palladium and platinum and then drying and calcining the wash-coated ceramic substrate.

【Claim 6】

The catalyst according to claim 5, wherein the catalytic solution comprises H_2PtCl_6 as a platinum precursor.

【DRAWINGS】

【Figure 1】



【Figure 2】

