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(54) METHOD FOR REACTIVATION OF PLATINUM GROUP METAL CATALYST



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(71) We, OSAKA GAS COMPANY, LTD., a Japanese company of 1, 5-chome, Hiranomachi, Higashi-ku, Osaka-shi, Osaka-fu, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for reactivation of a platinum group metal catalyst. More particularly, it relates to a method for reactivation of a platinum group metal catalyst whose catalytic activity is reduced as the result of having been used for catalytic reaction of hydrocarbons or compounds of carbon, hydrogen and oxygen. (CH or CHO compounds).

Conventional catalysts used for such reactions (e.g., steam-reforming of hydrocarbons, hydrocracking of hydrocarbons, partial oxidation of hydrocarbons and steam-reforming of alkanols, include base metal (e.g. Fe, Ni, Co) catalysts and noble metal (e.g. Pt, Pd, Ru) catalysts. In comparison with base metal catalysts (particularly nickel catalysts), noble metal catalysts (particularly platinum group metal catalysts) have some advantages such as resistance to deposition of carbonaceous materials thereon and maintenance of high catalytic activity with their use in small amounts. But, due to the cost of noble metals, practical use has been concentrated in base metal catalysts. In order to overcome the said defect, attempt has been made to reactivate the noble metal catalysts of reduced catalytic activity so as to enable their reuse. Typical conventional procedures for such reactivation are treatment with hydrogen, steam or oxygen, and in fact, this is quite effective in elimination of some certain poisonous materials including carbonaceous materials deposited on the catalysts. However, the recovery of the catalytic activity by those procedures is frequently not satisfactory.

In general, catalytic reactions of CH or CHO compounds in the presence of a platinum group metal catalyst result in deposition of various materials such as carbonaceous materials and sulfurous materials on the catalyst particles, as well as sintering of the catalyst particles causing their mutual cohesion whereby the particle size of the catalyst becomes larger and the dispersibility of the catalyst is thus lowered. Furthermore, the physical and chemical constitution and behaviour may be gradually changed during the catalytic reactions. Due to these and other factors which are still unclear, the catalytic activity of the catalyst is lowered with the progress of the catalytic reaction. For recovery of the catalytic activity to a satisfactory extent, it is necessary to remove substantially the effects of such factors.

As the result of extensive study, it has now been found that treatment of a platinum group metal catalyst whose activity is lowered as the result of having been used for catalytic steam reforming, hydro-cracking or partial oxidation of CH or CHO compounds with one or more suitable inorganic compounds and/or reducing substances in an aqueous medium can be effective for recovery of the catalytic activity. It has also been found that the combination of treatment with a suitable inorganic substance in an aqueous medium and with a reducing substance in an aqueous medium can be

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particularly effective for accomplishment of the reactivation. It has further been found that reactivation by such treatment with one or more inorganic substances and/or reducing substances can be more assured by carrying out treatment with hydrogen, steam or oxygen before or after the said treatment.

5 It may be noted that conventional treatment with hydrogen, steam or oxygen is effective in removal of carbonaceous materials deposited on the catalyst but not in elimination of sulfurous materials, while treatment with a suitable inorganic substance or a reducing substance can be effective in removal of sulfurous materials though the effect for elimination of carbonaceous materials may be not so high as seen in the conventional treatment. Particularly notable is that the conventional treatment is almost ineffective in recovery of the lowered catalytic activity while the treatment with a suitable inorganic compound or a reducing substance can be significantly effective for the reactivation. 10

15 According to the present invention, there is provided a method for reactivation of a platinum group metal catalyst whose activity has been reduced as a result of its use to catalyze one of the following processes, the substrate being one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen: 15

- (a) steam-reforming;
- (b) hydro-cracking; and
- (c) partial oxidation to produce a combustible gaseous mixture usable as a fuel gas, 20

25 said method comprising the step of treating the platinum group metal catalyst of reduced catalytic activity in an aqueous medium with at least one inorganic alkali metal or alkaline earth metal compound and/or at least one reducing substance, so that the catalytic activity of the catalyst is at least partially recovered. 25

30 The platinum group metal catalyst to be subjected to the treatment in the present invention may comprise at least one platinum group metal (ie. ruthenium, rhodium, palladium, osmium, iridium and platinum) as the catalyst component deposited on a carrier material such as alumina, magnesia, zirconia, titania, silica, silica-alumina, silica-magnesia, alumina-magnesia or carbon. In addition to the essential catalyst component, the platinum group metal catalyst may comprise any additive which does not materially have any unfavorable influence thereon. Examples of such additives include material known as the "co-catalysts" such as alkali metals, alkaline earth metals, iron, copper, nickel, cobalt, chromium, tungsten, manganese or molybdenum. Examples of organic compounds whose catalytic reactions can give rise to the deactivated catalysts with which this invention is concerned include aliphatic hydrocarbons, aromatic hydrocarbons, naphthenic hydrocarbons, alkanols and alkanones. Examples of the catalytic reaction are steam-reforming of hydrocarbons, hydro-cracking of hydrocarbons, partial oxidation of hydrocarbons to produce fuel gas, and steam-reforming of alkanols. 40

45 The said inorganic compound which may be used is an inorganic compound containing at least one of alkali metals and alkaline earth metals. Examples of the alkali metals and the alkaline earth metals are sodium, potassium, calcium, magnesium, barium, and strontium. Preferred examples of the inorganic compounds are hydroxides, carbonates, nitrates, and sulfates, etc. The concentration of the inorganic compound in the aqueous medium may be varied with the amount of the catalyst component deposited on the carrier material, the degree of loss of the catalytic activity, the temperature and pressure in the reactivation treatment and the like, and it may be usually from 0.001 to 10 N, preferably from 0.001 to 5 N. 45

50 As the reducing substance, there may be employed hydrazine, formaldehyde, sodium borohydride, lithium aluminum hydride, sodium tartrate, potassium tartrate, sodium potassium tartrate, calcium tartrate, sodium hydrogen tartrate, sodium formate, potassium formate, calcium formate, glucose, etc. The concentration of the reducing substance in the aqueous medium depends on factors including the amount of the catalyst component deposited on the carrier material, the degree of loss of the catalytic activity, and the temperature and pressure in the reactivation treatment. It may be normally from about 0.01% to 10% by weight. 50

55 Even when the deactivated catalyst is treated solely with the said inorganic compound or the reducing substance, appreciable elimination of sulfurous materials deposited on the catalyst and considerable recovery of the catalytic activity can be attained by choosing appropriate conditions for the treatment. In general, however, the treatment is preferably carried out in two steps, i.e. by treatment with the said inorganic compound and then treatment with the reducing substance, or vice versa. 60

When desired, such two step treatment may be repeatedly applied until a satisfactory recovery of the catalytic activity is achieved, though a single application of the two step treatment is usually sufficient.

5 The treatment with the inorganic compound is usually effected at room tempera- 5
ture (i.e. about 5 to 30°C) or while heating under atmospheric pressure or an elevated
pressure, suitable conditions vary greatly with factors such as the extent of the loss
of catalytic activity, the composition of the catalyst, and the nature of the said
10 inorganic compound. In general, a higher temperature can afford a better result, but
too high a temperature should be avoided since the carrier material might then be
10 dissolved. Thus, the temperature is usually from about 5 to 250°C, preferably from
about 50 to 200°C. The pressure may be appropriately decided so as to maintain
the system for treatment in a liquid state, and it does not usually exceed 50 kg/cm².

15 The treatment with the reducing substance may be carried out at a temperature
from room temperature to the decomposing temperature of the reducing substance
15 under atmospheric pressure or at an elevated pressure. Although the temperature is
considerably effected with various factors such as the decreased extent of the catalytic
activity, the composition of the catalyst and the kind of the reducing substance, the
temperature is ordinarily between room temperature and about 250°C, insofar as the
20 reducing substance is not decomposed. The pressure may be appropriately decided
so as to keep the system in a liquid state and is normally not higher than 50 kg/cm². 20

When treatment with the said inorganic compound or compounds and treatment
with a reducing substance are both used, there may be water-washing and/or drying
between them.

25 The treatment(s) with the inorganic compound and/or with the reducing substance
may be effected until a satisfactory recovery of the catalytic activity is attained. 25
Usually, the treatment(s) so as to eliminate not less than about 40% of carbonaceous
materials and not less than about 70% of sulfurous materials deposited on the catalyst
will achieve the satisfactory recovery of the catalytic activity. However, as stated above,
30 the deterioration of the catalytic activity is caused not only by deposition of
carbonaceous and/or sulfurous materials but also by other unclear factors, and there-
30 fore the elimination of the said deposited materials may not always be sufficient for
recovery of the catalytic activity.

35 If necessary, the said treatments with the inorganic compound and/or with the
reducing substance may be carried out in combination with any conventional reactiva- 35
tion treatment. For instance, the treatment of the catalyst with hydrogen, steam or
oxygen may be effected prior to, between or subsequently to the treatment(s) with
the inorganic compound and/or with the reducing substance.

40 Examples of usable gases are hydrogen, oxygen, steam, a mixture of hydrogen and
steam, and a mixture of oxygen and steam. These gases may be optionally diluted with
any inert gas such as nitrogen, helium or argon. Particularly preferred are (1) 40
hydrogen, (2) a mixture of hydrogen and steam having a hydrogen content of not
less than about 30 mol%, (3) a mixture of steam and a gaseous diluent having a
steam content of not less than about 30 mol%, (4) a mixture of oxygen and a gaseous
45 diluent having an oxygen content of not less than about 0.5% by volume, (5) a mixture
of oxygen, steam and a gaseous diluent having an oxygen content of not less than about
45 0.5% by volume and a steam content of not less than about 30% by volume, etc.

50 The conditions for treatment with the said gases depend on the amount of the
catalyst component deposited on the carrier material, the deposited amount of poisonous
materials (particularly carbonaceous materials), the concentration of the active gases,
50 the kind of other treatment procedures, etc., and usually a temperature of about 350
to 750°C and a pressure of about 1 to 50 atm. (absolute) are adopted. The treatment
may be continued until the deposited amount of poisonous materials, particularly
carbonaceous materials, is appreciably decreased. When the deposited amount of
55 carbonaceous materials is relatively large, the generation of heat may be significant.
In such cases, the oxygen content in the treating gases may be decreased or the use
55 of the treating gases containing no oxygen is preferred.

60 After the finalization of the treatment(s) as explained above, the resulting catalyst
may be washed with water and/or dried. Particularly, when the final step is the
60 treatment with the inorganic compound or the reducing agent in an aqueous medium,
water washing and drying are desirable.

As stated above, the thus reactivated catalyst can show satisfactorily recovered
catalytic activity. Even when the catalyst has been severely poisoned so that its catalytic
activity has been greatly lowered, the repeated application of the above treatment(s)

enables the recovery of the catalytic activity to a level nearly equal to that of a freshly prepared catalyst. Furthermore, when the activity of a once reactivated catalyst is lowered again repeated application of the above treatment(s) can reactivate it again. Thus, the present invention is quite advantageous in making it possible to use an expensive platinum group metal catalyst repeatedly.

Practical and presently preferred embodiments of the present invention are illustrated in the following Examples wherein part(s) and % are by weight unless otherwise indicated. The amount of the catalyst indicated as required for reaction is a minimum amount of the catalyst required to show a catalytic activity for reaction.

Example 1.

A catalyst comprising 2.0% of ruthenium and 0.1% of chromium oxide deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (hereinafter referred to as "Catalyst A₁") (325 ml) was charged into a tubular reactor of 1 inch in diameter, and a gaseous mixture comprising naphtha (content of sulfur, 2 ppm; final boiling point, 168°C), steam, hydrogen, methane and carbon oxides was fed therein to effect a continuous steam-reforming reaction for 1500 hours under the following conditions:

Temperature of reactor: inlet, 450°C, outlet, 524°C;

Space velocity: 2000 (1/hr);

Ratio of steam/hydrocarbon: 0.9 (number of oxygen atoms per one carbon atom in the gaseous feed mixture);

Pressure: 13 atm. (absolute)

After 1500 hours, the resultant catalysts (hereinafter referred to as "Catalyst B₁") was treated under the conditions as shown in Table 1 for reactivation. The reactivated catalyst was reused in a steam-reforming reaction under the same conditions as were mentioned above. The results are shown in Table 1.

As Table 1 shows, the reactivation treatment with hydrogen is extremely effective for elimination of carbonaceous materials, but removal of sulfurous materials is insufficient and dispersibility may be hardly recovered to that recovery of the catalytic activity is scarcely observed (Catalysts C₁-1 and C₁-2). With treatment with an inorganic alkaline substance, elimination of sulfurous materials and recovery of the dispersibility as well as recovery of the catalytic activity are good.

TABLE 1

Catalyst		A ₁	B ₁	Reactivated					
Conditions of treatment for reactivation		C ₁ -1	C ₁ -2	D ₁ -1	D ₁ -2	D ₁ -3	D ₁ -4	D ₁ -5	D ₁ -6
Reactivating agent		H ₂	O ₂ :N ₂ (= 21:79 by volume)	0.375N NaOH	0.375N NaOH	0.375N NaOH	1.0N NaOH	5.0N NaOH	0.375N Na ₂ CO ₃
Temperature (°C)		650	500	50	70	100	100	70	100
Pressure (ata)		6.0	6.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)		12	5	6.0	3.0	1.5	0.75	0.5	3.0
Post-treatment		—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.					
Elimination percentage of poisonous materials (%)		100	100	41	46	55	54	59	54
Sulfurous materials		33	40	78	84	95	97	100	93
Specific surface area (m ² /g-Ru)		19	17	28	30	35	37	37	36
Amount of catalyst required for reaction (ml)		—	—	85	68	63	63	61	64

TABLE 1 (Continued)

Catalyst		Reactivated					
		D ₁ -7	D ₁ -8	D ₁ -9	D ₁ -10	D ₁ -11	D ₁ -12
Conditions of treatment for reactivation	Reactivating agent	0.375N KOH	0.375N Ba(OH) ₂	0.375N Sr(OH) ₂	0.375N NaOH	0.375N NaOH	0.001N NaOH
	Temperature (°C)	100	100	100	148	205	100
	Pressure (ata)	1.0	1.0	1.0	5.0	20.0	1.0
	Time (hrs)	3.0	3.0	3.0	1.0	0.5	10.0
	Post-treatment	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.					
Elimination percentage of poisonous materials (%)	Carbonaceous materials	52	50	48	56	58	40
	Sulfurous materials	90	87	87	100	100	80
Specific surface area (m ² /g-Ru)		35	33	32	34	37	30
Amount of catalyst required for reaction (ml)		64	66	68	63	60	69

Example 2.

A catalyst comprising 0.3% of ruthenium deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (1000 ml) was charged into a tubular reactor of 1 inch in diameter, and naphtha (final boiling point, 108°C) and hydrogen were fed therein to effect a continuous hydro-cracking reaction under the following conditions:

Temperature of reactor at inlet: 265°C;

Pressure: 46 atm. (absolute);

Ratio of hydrogen/hydrocarbon: 1.20 (by mol)

Mass velocity: 500 kg-mol/m².hr

The conversion of hydrogen at the initial stage was 82%, and the catalytic activity was materially decreased after about 200 hours. The resultant catalyst was heated in a 0.375 N aqueous solution of sodium hydroxide at 100°C for 3 hours, washed with water at 100°C for 2 hours and then dried at 100°C for 16 hours. The thus reactivated catalyst was reused for hydro-cracking under the same conditions as above, and a conversion of hydrogen of 80% was observed.

Example 3.

A catalyst comprising 2.6% of ruthenium and 0.1% of chromium oxide deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (hereinafter referred to as "Catalyst A₂") (325 ml) was charged into a tubular reactor of 1 inch in diameter, and a gaseous mixture comprising naphtha (content of sulfur, 2 ppm; final boiling point, 168°C), steam, hydrogen, methane and carbon oxides was fed therein to effect a continuous steam-reforming reaction for 2400 hours under the following conditions:

Temperature of reactor: inlet, 400°C, outlet, 517°C;

Space velocity: 1500 (1/hr);

Ratio of steam/hydrocarbon: 0.7 (number of oxygen atoms per one carbon atom in the gaseous feed mixture);

Pressure: 13 atm. (absolute)

After 2400 hours, the resultant catalyst (hereinafter referred to as "Catalyst B₂") was treated under the conditions as shown in Table 2 for reactivation. The reactivated catalyst was reused in steam-reforming reaction under the same conditions as mentioned above. The results are shown in Table 2.

As Table 2 shows, the reactivation treatment with hydrogen is extremely effective for elimination of carbonaceous materials, but removal of sulfurous materials is

insufficient and the dispersibility may be hardly recovered so that recovery of the catalytic activity is scarcely observed (Catalyst C₂). With treatment with an inorganic alkaline substance at room temperature, elimination of sulfurous materials and recovery of the dispersibility are relatively good when the treatment time is long, but the recovery of the catalytic activity is insufficient (Catalysts D₂-1 and D₂-2). Treatment with an inorganic alkaline substance under heating is proved to be effective for recovery of the catalytic activity (Catalysts D₂-3 to D₂-5). In treatment with a reducing substance elimination of sulfurous material is good, but removal of carbonaceous materials is scarcely achieved. There is a tendency to recovery of the catalytic activity (Catalysts D₂-6 to D₂-13).

TABLE 2

Catalyst	A ₂	B ₂	C ₂	Reactivated						
				D ₂ -1	D ₂ -2	D ₂ -3	D ₂ -4	D ₂ -5	D ₂ -6	D ₂ -7
Reactivating agent	—	—	H ₂	0.375N NaOH	0.375N NaOH	0.375N NaOH	0.375N NaOH	0.375N NaOH	0.4% Hydrazine	0.3% Lithium aluminum hydride
Temperature (°C)	—	—	650	30	30	50	100	148	20	20
Pressure (ata)	—	—	6.0	1.0	1.0	1.0	1.0	5.0	1.0	1.0
Time (hrs)	—	—	12.0	3.0	10.0	6.0	3.0	1.0	3.0	3.0
Post-treatment	—	—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.						
Elimination percentage of poisonous materials (%)	—	—	100	12	41	43	52	56	0	0
	—	—	31	32	72	78	90	100	68	49
Specific surface area (m ² /g-Ru)	43	17	17	21	27	28	34	35	21	23
Amount of catalyst required for reaction (ml)	92	—	—	—	—	147	110	106	276	270

TABLE 2 (Continued)

Catalyst		Reactivated					
		D ₂ -8	D ₂ -9	D ₂ -10	D ₂ -11	D ₂ -12	D ₂ -13
Conditions of treatment for reactivation	Reactivating agent	0.7% Sodium tartrate	2.0% Sodium formate	0.3% Glucose	1.0% Hydra-zine	1.0% Formal-dehyde	1.0% Sodium boro-hydride
	Temperature (°C)	20	20	20	60	60	60
	Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0
	Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0
	Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.					
Elimination percentage of poisonous materials (%)	Carbonaceous materials	0	0	0	0	0	0
	Sulfurous materials	46	53	49	90	67	88
Specific surface area (m ² /g-Ru)		23	23	23	23	23	23
Amount of Catalyst required for reaction (ml)		272	272	276	266	270	276

Example 4.

5 The reactivated catalysts obtained in Example 3 (Catalysts D₂-1 to D₂-12) were each subjected to further treatment for reactivation under the conditions as shown in Table 3. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as in Example 3. The results are shown in Table 3. 5

10 As understood from Table 3, the catalysts (E₃-1 to E₃-20) reactivated in two steps are much more recovered in the catalytic activity than the catalysts (D₂-1 to D₂-12) reactivated in one step. 10

TABLE 3

Catalyst	E ₃ -1	E ₃ -2	E ₃ -3	E ₃ -4	E ₃ -5	E ₃ -6	E ₃ -7	E ₃ -8	E ₃ -9	E ₃ -10
Catalyst used	D ₂ -1	D ₂ -2	D ₂ -3	D ₂ -3	D ₂ -4	D ₂ -4	D ₂ -6	D ₂ -6	D ₂ -11	D ₂ -12
Reactivating agent	1.0% Hydrazine	0.4% Hydrazine	0.4% Hydrazine	0.5% Formaldehyde	0.4% Hydrazine	0.3% Sodium borohydride	0.375N NaOH	0.375N NaOH	0.375N NaOH	0.375N NaOH
Temperature (°C)	60	20	20	20	20	20	50	100	100	80
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	6.0	3.0	3.0	3.0
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.					Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.				
Elimination percentage of poisonous materials (%)	12	41	43	43	52	52	43	54	53	47
Specific surface area (m ² /g-Ru)	89	91	93	93	97	95	91	97	95	89
Amount of catalyst required for reaction (ml)	34	36	36	36	40	40	35	39	41	39
	108	110	102	106	95	98	102	95	93	95

TABLE 3 (Continued)

Catalyst	E ₃ -11	E ₃ -12	E ₃ -13	E ₃ -14	E ₃ -15	E ₃ -16	E ₃ -17	E ₃ -18	E ₃ -19	E ₃ -20
Catalyst used	D ₂ -1	D ₂ -2	D ₂ -3	D ₂ -3	D ₂ -4	D ₂ -4	D ₂ -7	D ₂ -8	D ₂ -9	D ₂ -10
Conditions of treatment for reactivation	0.3% Lithium aluminum hydride	0.3% Lithium aluminum hydride	0.7% Sodium tartrate	2.0% Sodium formate	0.3% Lithium aluminum hydride	0.3% Glucose	0.375N NaOH	0.1N NaOH	0.375N NaOH	0.375N NaOH
Temperature (°C)	20	20	20	20	20	20	50	100	100	80
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	6.0	3.0	1.5	3.0
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16-hrs.									
Elimination percentage of poisonous materials (%)	12	41 ¹	43	43	52	52	43	44	46	47
Specific surface area (m ² /g-Ru)	66	86	89	90	95	95	89	88	93	92
Amount of catalyst required for reaction (ml)	31	36	37	37	41	40	38	37	37	37
	126	106	100	100	94	95	98	100	100	100
	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.									

Example 5.

The reactivated catalyst obtained in Example 3 (Catalyst D₂-3) was treated with a 0.4% aqueous solution of hydrazine at 20°C under 1 atm. (absolute) for 3 hours, washed with water at 75°C for 3 hours and dried at 100°C for 16 hours. Then, the resulting catalyst was again subjected to treatment with a 0.375 N aqueous solution of sodium hydroxide at 50°C under 1 atm. (absolute) for 6 hours and then treatment with a 0.4% aqueous solution of hydrazine at 20°C under 1 atm. (absolute) for 3 hours, followed by washing with water at 75°C for 3 hours and drying at 100°C for 16 hours. The thus reactivated catalyst used for steam-reforming under the same conditions as stated in Example 3. The results are as follows: elimination percentage

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of poisonous materials: carbonaceous materials, 75%; sulfurous material, 100%. Specific surface area: 42 m²/g-Ru. Amount of catalyst required for reaction: 93 ml.

As the above results show, repeated treatments with an inorganic alkaline substance and with a reducing substance are quite effective for reactivation of the catalyst.

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Example 6.

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The reactivated catalyst obtained in Example 3 (Catalyst D₂-3) was treated with a 0.7% aqueous solution of sodium tartrate at 20°C under 1 atm. (absolute) for 3 hours, washed with water at 75°C for 3 hours and dried at 100°C for 16 hours. Then, the resulting catalyst was again subjected to treatment with a 0.375 N aqueous solution of sodium hydroxide at 50°C under 1 atm. (absolute) for 6 hours and then treatment with a 0.7% aqueous solution of sodium tartrate at 20°C under 1 atm. (absolute) for 3 hours, followed by washing with water at 75°C for 3 hours and drying at 100°C for 16 hours. The thus reactivated catalyst was used for steam-reforming under the same conditions as stated in Example 3. The results are as follows: elimination percentage of poisonous materials: carbonaceous materials, 70%; sulfurous material, 100%. Specific surface area: 42 m²/g-Ru. Amount of catalyst required for reaction: 93 ml.

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As the above results show, the repeated treatments with an inorganic alkaline substance and with a reducing substance are quite effective for reactivation of the catalyst.

Example 7.

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A catalyst comprising 3.8% of ruthenium deposited on spheroidal particles of alumina of 4 mm in diameter (hereinafter referred to as "Catalyst A₁") (325 ml) was charged into a tubular reactor of 1 inch in diameter, and naphtha (content of sulfur, 2 ppm; final boiling point, 220°C) and steam were fed therein to effect a continuous steam-reforming reaction for 750 hours under the following conditions:

Temperature of reactor: inlet, 510°C, outlet, 518°C;

Space velocity: 2000 (1/hr);

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Ratio of steam/hydrocarbon: 1.9 (number of oxygen atoms per one carbon atom in the gaseous feed materials);

Pressure: 13 atm. (absolute)

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After 750 hours, the catalyst (hereinafter referred to as "Catalyst B₄") was treated under the same conditions as shown in Table 4 for reactivation. The reactivated catalyst was reused in steam-reforming reaction under the same conditions as mentioned above. The results are shown in Table 4.

As Table 4 shows, treatment with an inorganic alkaline substance produces recovery of the catalytic activity, and treatment with a reducing substance shows a tendency to recovery of the catalytic activity.

TABLE 4

Catalyst	A ₄	B ₄	C ₄	Reactivated					
				D ₄ -1	D ₄ -2	D ₄ -3	D ₄ -4	D ₄ -5	D ₄ -6
Reactivating agent	—	—	H ₂	0.375N NaOH	0.375N NaOH	0.375N NaOH	0.4% Hydrazine	1.0% Formaldehyde	1.0% Sodium borohydride
Temperature (°C)	—	—	650	30	50	100	20	60	60
Pressure (ata)	—	—	6.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	—	—	12.0	3.0	6.0	3.0	3.0	3.0	3.0
Post-treatment	—	—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.					
Elimination percentage of poisonous materials (%)	—	—	100	10	41	56	0	0	0
Sulfurous materials	—	—	29	30	80	94	72	71	90
Specific surface area (m ² /g-Ru)	43	20	19	23	29	36	23	26	26
Amount of catalyst required for reaction (ml)	91	—	—	—	145	109	270	264	270

TABLE 4 (Continued)

Catalyst		Reactivated													
		D ₄ -7	D ₄ -8	D ₄ -9	D ₄ -10	D ₄ -11	D ₄ -12	D ₄ -13	D ₄ -14	D ₄ -15					
Conditions of treatment for reactivation	Reactivating agent	0.375N Na ₂ CO ₃	0.375N Ba(OH) ₂	0.375N Sr(OH) ₂	0.1N Na ₂ CO ₃	0.375N Ba(OH) ₂	0.375N Sr(OH) ₂	0.5% Formaldehyde	0.3% Sodium borohydride	0.3% Lithium aluminum hydride					
	Temperature (°C)	100	100	100	100	80	100	20	20	20					
	Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0					
	Time (hrs)	3.0	3.0	3.0	3.0	3.0	1.0	3.0	3.0	3.0					
	Post-treatment	Water washing: 100°C, 2 hrs Drying: 100°C, 16 hrs.										Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.			
Elimination percentage of poisonous materials (%)	Carbonaceous materials	54	51	50	44	49	46	0	0	0					
	Sulfurous materials	91	89	86	77	80	79	56	70	51					
	Specific surface area (m ² /g-Ru)	36	35	35	32	32	31	23	23	26					
	Amount of catalyst required for reaction (ml)	111	114	119	123	126	129	274	278	260					

TABLE 4 (Continued)

Catalyst		Reactivated		
		D ₄ -16	D ₄ -17	D ₄ -18
Conditions of treatment for reactivation	Reactivating agent	0.7% Sodium tartrate	2.0% Sodium formate	0.3% Glucose
	Temperature (°C)	20	20	20
	Pressure (ata)	1.0	1.0	1.0
	Time (hrs)	3.0	3.0	3.0
	Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.		
Elimination percentage of poisonous materials (%)	Carbonaceous materials	0	0	0
	Sulfurous materials	49	57	52
Specific surface area (m ² /g-Ru)		26	25	23
Amount of catalyst required for reaction (ml)		264	264	270

Example 8.

The reactivated catalysts as obtained in Example 7 (Catalysts D₄-1 to D₄-18) were each subjected to further treatment for reactivation under the conditions as shown in Table 5. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as were employed in Example 7. The results are shown in Table 5.

As Table 5 shows, the catalysts (E₅-1 to E₅-19) reactivated in two steps are recovered in the catalytic activity to a much greater extent than the catalysts (D₄-1 to D₄-18) reactivated in one step.

TABLE 5

Catalyst	E ₅ -1	E ₅ -2	E ₅ -3	E ₅ -4	E ₅ -5	E ₅ -6	E ₅ -7	E ₅ -8	E ₅ -9	E ₅ -10	
Catalyst used	D ₄ -1	D ₄ -3	D ₄ -8	D ₄ -8	D ₄ -10	D ₄ -11	D ₄ -12	D ₄ -13	D ₄ -13	D ₄ -14	
Conditions of treatment for reactivation	1.0% Sodium boro-hydride	0.4% Hydrazine	0.5% Formaldehyde	0.5% Formaldehyde	0.5% Formaldehyde	1.0% Hydrazine	0.3% Sodium boro-hydride	0.375N NaOH	0.1N NaOH	0.375N KOH	
Temperature (°C)	60	20	20	60	20	60	20	100	100	80	
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.										
Elimination percentage of poisonous materials (%)	Carbonaceous materials	10	56	51	51	44	49	46	54	44	52
	Sulfurous materials	86	96	95	97	89	96	90	86	80	85
Specific surface area (m ² /g-Ru)	36	41	41	41	36	41	35	41	36	36	
Amount of catalyst required for reaction (ml)	109	93	97	93	106	97	116	95	102	106	

TABLE 5 (Continued)

Catalyst	E ₅ -11	E ₅ -12	E ₅ -13	E ₅ -14	E ₅ -15	E ₅ -16	E ₅ -17	E ₅ -18	D ₅ -19	
Catalyst used	D ₄ -1	D ₄ -2	D ₄ -10	D ₄ -11	D ₄ -12	D ₂ -15	D ₄ -16	D ₄ -17	D ₄ -18	
Conditions of treatment for reactivation	0.7% Sodium tartrate	0.3% Glucose	0.3% Lithium aluminum hydride	2.0% Sodium formate	0.3% Lithium aluminum hydride	0.1N NaOH	0.1N Na ₂ CO ₃	0.375N Ba(OH) ₂	0.375N Sr(OH) ₂	
Temperature (°C)	20	20	20	20	20	100	100	80	100	
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	1.0	
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.					Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.				
Elimination percentage of poisonous materials (%)	10	41	44	49	46	47	44	49	46	
	65	91	89	91	90	90	88	91	90	
Specific surface area (m ² /g-Ru)	32	37	40	37	36	41	40	37	35	
Amount of catalyst required for reaction (ml)	123	102	98	102	106	96	100	102	112	

Example 9.

The reactivated catalyst obtained in Example 7 (Catalyst D₄-13) was treated with a 0.1 N aqueous solution of sodium hydroxide at 100°C under 1 atm. (absolute) for 3 hours, washed with water at 100°C for 2 hours and dried at 100°C for 16 hours. Then, the resulting catalyst was again subjected to treatment with a 0.5% aqueous solution of formaldehyde at 20°C under 1 atm. (absolute) for 3 hours and treatment with a 0.1 N aqueous solution of sodium hydroxide at 100°C under 1 atm. (absolute) for 3 hours, followed by washing with water at 100°C for 2 hours and drying at 100°C for 16 hours. The thus reactivated catalyst was used for steam-reforming under the same conditions as stated in Example 7. The results are as follows: elimination percentage of poisonous materials: carbonaceous materials, 80%; sulfurous material, 100%. Specific surface area: 42 m²/g-Ru. Amount of catalyst required for reaction: 92 ml.

As the above results show, the repeated treatments with a reducing substance and with an inorganic alkaline substance are quite effective for reactivation of the catalyst.

Example 10.

The reactivated catalyst obtained in Example 7 (Catalyst D₄-17) was treated with a 0.375 N aqueous solution of barium hydroxide at 80°C under 1 atm. (absolute) for 3 hours, washed with water at 100°C for 2 hours and dried at 100°C for 16 hours. Then, the resulting catalyst was again subjected to treatment with a 2.0% aqueous solution of sodium formate at 20°C under 1 atm. (absolute) for 3 hours and treatment with a 0.375 N aqueous solution of barium hydroxide at 80°C under 1 atm. (absolute) for 3 hours, followed by washing with water at 100°C for 2 hours and drying at 100°C for 16 hours. The thus reactivated catalyst was used for steam-reforming under the same conditions as stated in Example 7. The results are as follows: elimination percentage of poisonous materials: carbonaceous materials, 76%; sulfurous material, 100%. Specific surface area: 42 m²/g-Ru. Amount of catalyst required for reaction 92 ml.

As these results show, the repeated treatments with an inorganic alkaline substance and with a reducing substance are quite effective for reactivation of the catalyst.

Example 11.

The reactivated catalysts obtained in Example 4 (Catalyst E₃-5) and in Example 4 (Catalyst E₃-7) were each reused for steam-reforming under the same conditions as shown in Example 3. The results are shown in Table 6, from which it can be seen that the reactivated catalysts show similar behaviour to the fresh catalyst (Catalyst A₂) in depression of the catalytic activity, and that their catalytic activity, particularly that of Catalyst E₃-5, is nearly equal to the catalytic activity of the fresh catalyst.

TABLE 6

Catalyst		A ₂	E ₃ -5	E ₃ -7
Amount of catalyst required for reaction (ml)	Start	92	95	102
	600 hours	164	171	183
	1200 hours	221	232	250

Example 12.

The reactivated catalysts obtained in Example 4 (Catalyst E₃-13) and in Example 6 were each reused for steam-reforming under the same conditions as described for Example 3. The results are shown in Table 7, from which it can be seen that the reactivated catalysts show similar behaviour to the fresh catalyst (Catalyst A₂) in depression of the catalytic activity, and that their catalytic activity, particularly that of the reactivated catalyst obtained in Example 6, is nearly equal to the catalytic activity of the fresh catalyst.

TABLE 7

Catalyst		A ₂	E ₃ -13	Obtained in Example 6
Amount of catalyst required for reaction (ml)	Start	92	100	93
	600 hours	164	179	166
	1200 hours	221	242	224

Example 13.

The reactivated catalysts obtained in Example 8 (Catalyst E₃-8) and in Example 9 were each reused for steam-reforming under the same conditions as shown in Example 7. The results are shown in Table 8, from which it can be understood that the reactivated catalysts show similar behaviour to the fresh catalyst (Catalyst A₄) in depression of the catalytic activity.

TABLE 8

Catalyst		A ₄	E ₅ -8	Obtained in Example 9
Amount of catalyst required for reaction (ml)	Start	91	95	92
	200 hours	156	167	159
	400 hours	222	238	226

Example 14.

The reactivated catalysts obtained in Example 8 (Catalyst E₅-16) and in Example 10 were each reused for steam-reforming under the same conditions as shown in Example 7. The results are shown in Table 9, from which it can be seen that the reactivated catalysts show similar behavior to the fresh catalyst (Catalyst A₄) in depression of the catalytic activity.

TABLE 9

Catalyst		A ₄	E ₅ -16	Obtained in Example 10
Amount of catalyst required for reaction (ml)	Start	91	96	92
	200 hours	156	166	160
	400 hours	222	235	229

Example 15.

A catalyst comprising 2.0% of ruthenium and 0.1% of chromium oxide deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (hereinafter referred to as "Catalyst A₁₀") (325 ml) was charged into a tubular reactor of 1 inch in diameter, and a gaseous mixture comprising naphtha (content of sulfur, 2 ppm; final boiling point, 168°C), steam, hydrogen, methane and carbon oxides was fed therein to effect a continuous steam-reforming reaction for 1500 hours under the following conditions:

Temperature of reactor: inlet, 450°C, outlet, 524°C;

Space velocity: 2000 (1/hr);

Ratio of steam/hydrocarbon: 0.9 (number of oxygen atoms per one carbon atom in the feeding gaseous mixture);

Pressure: 13 atm. (absolute)

After 1500 hours, the resultant catalyst (hereinafter referred to as "Catalyst B₁₀") was treated under the conditions shown in Table 10 for reactivation. The reactivated

catalyst was reused in steam-reforming reaction under the same conditions as mentioned above. The results are shown in Table 10.

As Table 10 shows, the reactivation treatment with gaseous materials is effective for elimination of carbonaceous materials, but removal of sulfurous materials is insufficient and the dispersibility may be hardly recovered so that recovery of the catalytic activity is scarcely observed (Catalysts C₁₀₋₁ to C₁₀₋₅). With treatment with an inorganic alkaline substance, however, elimination of sulfurous materials and recovery of the dispersibility (as well as recovery of the catalytic activity) are good.

TABLE 10

Catalyst	A ₁₀	B ₁₀	Reactivated					D ₁₀₋₁	D ₁₀₋₂	D ₁₀₋₃
			C ₁₀₋₁	C ₁₀₋₂	C ₁₀₋₃	C ₁₀₋₄	C ₁₀₋₅			
Reactivating agent*)	—	—	H ₂	H ₂ :H ₂ O (=1:1 by mol)	H ₂ O:N ₂ (=3:1 by mol)	O ₂ :N ₂ (=21:79 by volume)	O ₂ :H ₂ O:N ₂ (=10:50:40 by volume)	0.375N NaOH	0.375N Na ₂ CO ₃	0.375N Ba(OH) ₂
Temperature (°C)	—	—	600	600	650	500	600	100	100	100
Pressure (ata)	—	—	6.0	6.0	6.0	6.0	6.0	1.0	1.0	1.0
Time (hrs)	—	—	6.0	6.0	12.0	5.0	10.0	1.5	3.0	3.0
Post-treatment	—	—	—	—	—	—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hours.		
Elimination percentage of poisonous materials (%)	—	—	78	80	100	100	100	55	54	50
Specific surface area (m ² /g-Ru)	43	20	19	19	19	17	18	35	36	33
Amount of catalyst required for reaction (ml)	52.5	—	—	—	—	—	—	63	64	66

Note: *) In case of Catalysts C₁₀₋₁ to C₁₀₋₅, the treatment was carried out with a space velocity of 2500 (1 hr).

TABLE 10. (Continued)

Catalyst		Reactivated	
		D ₁₀ -4	D ₁₀ -5
Conditions of treatment for reactivation	Reactivating agent	0.375N NaOH	0.375N NaOH
	Temperature (°C)	50	30
	Pressure (ata)	1.0	1.0
	Time (hrs)	6.0	10.0
	Post-treatment	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	
Elimination percentage of poisonous materials (%)	Carbonaceous materials	41	40
	Sulfurous materials	78	75
Specific surface area (m ² /g-Ru)		28	28
Amount of catalyst required for reaction (ml)		85	—

Example 16.

The reactivated catalysts as obtained in Example 15 (Catalysts C₁₀-1 to C₁₀-5) were each subjected to further treatment for reactivation under the conditions as shown in Table 11. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as shown in Example 15. The results are shown in Table 11.

Table 11 shows that, the catalysts (E₁₁-1 to E₁₁-6) reactivated in two steps are much recovered in their catalytic activity.

TABLE II

Catalyst	E ₁₁ -1	E ₁₁ -2	E ₁₁ -3	E ₁₁ -4	E ₁₁ -5	E ₁₁ -6	E ₁₁ -7	E ₁₁ -8
Catalyst used	C ₁₀ -1	C ₁₀ -1	C ₁₀ -1	C ₁₀ -1	C ₁₀ -2	C ₁₀ -5	C ₁₀ -1	C ₁₀ -1
Reactivating agent	0.375N NaOH	0.375N NaOH	0.375N Na ₂ CO ₃	0.375N Ba(OH) ₂	0.1N NaOH	0.375N NaOH	0.375N NaOH	0.375N NaOH
Temperature (°C)	50	80	100	100	100	80	30	30
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	3.0	1.5	1.5	2.0	1.5	1.5	10.0	3.0
Post-treatment	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.							
Elimination percentage of poisonous materials (%)	81	86	85	83	83	100	80	80
	83	96	94	88	90	97	80	48
Specific surface area (m ² /g-Ru)	31	38	37	35	37	38	28	23
Amount of catalyst required for reaction (ml)	78	58	61	63	61	58	-	-

Example 17.

The reactivated catalysts as obtained in Example 16 (Catalysts E₁₁-1, E₁₁-7 and E₁₁-8) were each subjected to further treatment for reactivation under the conditions as shown in Table 12. The thus reactivated catalysts were each reused for 5 continuous steam-reforming under the same conditions as shown in Example 15. The results are shown in Table 12.

Table 12 shows that, the catalysts (F₁₂-1 to F₁₂-11) reactivated in three steps are much recovered in their catalytic activity.

TABLE 12

Catalyst	F ₁₂ -1	F ₁₂ -2	F ₁₂ -3	F ₁₂ -4	F ₁₂ -5	F ₁₂ -6	F ₁₂ -7	F ₁₂ -8	F ₁₂ -9	F ₁₂ -10	F ₁₂ -11
Catalyst used	E ₁₁ -1	E ₁₁ -1	E ₁₁ -1	E ₁₁ -1	E ₁₁ -1	E ₁₁ -7	E ₁₁ -7	E ₁₁ -7	E ₁₁ -7	E ₁₁ -7	E ₁₁ -8
Reactivating agent	0.4% hydrazine	0.5% Formaldehyde	0.3% Sodium borohydride	0.3% Lithium aluminum hydride	0.3% Glucose	0.4% Hydrazine	0.5% Formaldehyde	0.3% Sodium borohydride	0.7% Sodium tartrate	2.0% Sodium formate	1.0% Hydrazine
Temperature (°C)	20	20	20	20	20	20	20	20	20	20	60
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.										
Elimination percentage of poisonous materials (%)	81	81	81	81	81	80	80	80	80	80	80
	96	90	95	92	92	92	87	90	91	93	94
Specific surface area (m ² /g-Ru)	41	40	40	40	40	37	36	35	36	36	39
Amount of catalyst required for reaction (ml)	53	55	56	53	56	60	61	63	61	61	56

Example 18.

The reactivated catalysts obtained in Example 16 (Catalyst E₁₁-2) and in Example 17 (Catalyst F₁₂-1) were each reused for steam-reforming under the same conditions as shown in Example 15. The results are shown in Table 13, from which it can be seen that the reactivated catalysts show similar behavior to the fresh catalyst (Catalyst A₁₀) in depression of the catalytic activity, and that their catalytic activity, particularly that of Catalyst F₁₂-1, is nearly equal to the catalytic activity of the fresh catalyst.

TABLE 13

Catalyst		A ₁₀	E ₁₁ -2	F ₁₂ -1
Amount of catalyst required for reaction (ml)	Start	52.5	58	53
	300 hours	123.5	139.5	125
	600 hours	183	208.5	186
	900 hours	252	289	257

Example 19.

A catalyst comprising 2.6% of ruthenium and 0.1% of chromium oxide deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (hereinafter referred to as "Catalyst A₁₀") in (325 ml) was charged into a tubular reactor of 1 inch in diameter, and a gaseous mixture comprising naphtha (content of sulfur, 2 ppm; final boiling point, 168°C), steam, hydrogen, methane and carbon oxides was fed therein to effect a continuous steam-reforming reaction for 2400 hours under the following conditions:

Temperature of reactor: inlet, 400°C, outlet, 517°C;

Space velocity: 1500 (l/hr);

Ratio of steam/hydrocarbon: 0.7 (number of oxygen atoms per one carbon atom in the gaseous feed mixture);

Pressure: 13 atm. (absolute)

After 2400 hours, the resultant catalyst (hereinafter referred to as "Catalyst B₁₄") was treated under the conditions as shown in Table 14 for reactivation. The reactivated catalyst was reused in steam-reforming reaction under the same conditions as mentioned above. The results are shown in Table 14.

Table 14 shows that, the reactivation treatment with gaseous materials is effective for elimination of carbonaceous materials, but removal of sulfurous materials is insufficient and the dispersibility may be hardly recovered so that recovery of the catalytic activity is scarcely observed (Catalysts C₁₄-1 to C₁₄-5). With treatment with an inorganic alkaline substance, elimination of sulfurous materials and recovery of the dispersibility (as well as recovery of the catalytic activity) are good.

TABLE 14

Catalyst	A ₁₄	B ₁₄	Reactivated							D ₁₄₋₁	D ₁₄₋₂	D ₁₄₋₃
			C ₁₄₋₁	C ₁₄₋₂	C ₁₄₋₃	C ₁₄₋₄	C ₁₄₋₅					
Conditions of treatment for reactivation	—	—	H ₂	H ₂ :H ₂ O (=1:1 by mol)	H ₂ O:N ₂ (=3:1 by mol)	O ₂ :N ₂ (=21:79 by volume)	O ₂ :H ₂ O:N ₂ (=10:50:40 by volume)	0.375N NaOH	0.375N NaOH	0.375N NaOH		
Temperature (°C)	—	—	600	600	650	500	600	600	30	30	50	
Pressure (ata)	—	—	6.0	6.0	6.0	6.0	6.0	6.0	1.0	1.0	1.0	
Time (hrs)	—	—	6.0	6.0	12.0	5.0	10.0	10.0	3.0	10.0	6.0	
Post-treatment	—	—	—	—	—	—	—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.			
Elimination percentage of poisonous materials (%)	—	—	75	78	100	100	100	100	12	41	43	
	—	—	19	25	30	37	35	35	32	72	78	
Specific surface area (m ² /g-Ru)	43	20	19	19	19	17	18	18	21	27	28	
Amount of catalyst required for reaction (ml)	92	—	—	—	—	—	—	—	—	—	147	

Note: *) In case of Catalysts C₁₄₋₁ to C₁₄₋₅, the treatment was carried out with a space velocity of 2500 (l/hr).

TABLE 14 (Continued)

Catalyst		Reactivated					
		D ₁₄ -4	D ₁₄ -5	D ₁₄ -6	D ₁₄ -7	D ₁₄ -8	D ₁₄ -9
Conditions of treatment for reactivation	Reactivating agent	0.375N NaOH	0.375N Na ₂ CO ₃	0.375N Ba(OH) ₂	0.1N NaOH	0.375N Na ₂ CO ₃	0.375N Ba(OH) ₂
	Temperature (°C)	100	100	100	100	80	100
	Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0
	Time (hrs)	3.0	3.0	3.0	3.0	3.0	1.5
	Post-treatment	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.					
Elimination percentage of poisonous materials (%)	Carbonaceous materials	52	51	47	40	44	45
	Sulfurous materials	90	88	82	75	77	76
Specific surface area (m ² /g-Ru)		34	34	32	30	30	29
Amount of catalyst required for reaction (ml)		110	112	116	120	122	127

Example 20.

5 The reactivated catalysts obtained in Example 19 (Catalysts D₁₄-7 to D₁₄-9) were each subjected to further treatment for reactivation under the conditions as shown in Table 15. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as described in Example 19. The results are shown in Table 15. 5

As Table 15 shows, the catalysts (E₁₅-1 to E₁₅-5) reactivated in two steps are much recovered in their catalytic activity.

TABLE 15

Catalyst		E ₁₅ -1	E ₁₅ -2	E ₁₅ -3	E ₁₅ -4	E ₁₅ -5
Catalyst used		D ₁₄ -7	D ₁₄ -7	D ₁₄ -7	D ₁₄ -8	D ₁₄ -9
Conditions of treatment for reactivation	Reactivating agent*	H ₂	H ₂ :H ₂ O (=1:1 by mol)	O ₂ :H ₂ O: N ₂ (=10:50:40 by volume)	H ₂	H ₂ :H ₂ O (=1:1 by mol)
	Temperature (°C)	600	600	600	600	650
	Pressure (ata)	6.0	6.0	6.0	6.0	6.0
	Time (hrs)	6.0	6.0	10.0	12.0	12.0
	Post-treatment	—	—	—	—	—
Elimination percentage of poisonous materials (%)	Carbonaceous materials	85	87	100	100	100
	Sulfurous materials	80	81	84	81	82
Specific surface area (m ² /g-Ru)		31	31	30	30	30
Amount of catalyst required for reaction (ml)		105	105	110	110	112

Note: *) In case of Catalysts E₁₅-1 to E₁₅-5, the treatment was carried out with a space velocity of 2500 (1/hr).

Example 21.

The reactivated catalysts obtained in Example 19 (Catalysts D₁₄-1 to D₁₄-4, D₁₄-8 and D₁₄-9) were each subjected to further treatment for reactivation under the conditions as shown in Table 16. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as described in Example 19. The results are shown in Table 16.

As Table 16 shows, the catalysts (E₁₆-1 to E₁₆-11) reactivated in two steps are much recovered in the catalytic activity.

TABLE 16

Catalyst	E _{1,6} -1	E _{1,6} -2	E _{1,6} -3	E _{1,6} -4	E _{1,6} -5	E _{1,6} -6	E _{1,6} -7	E _{1,6} -8	E _{1,6} -9	E _{1,6} -10
Catalyst used	D _{1,4} -1	D _{1,4} -2	D _{1,4} -3	D _{1,4} -3	D _{1,4} -3	E _{1,4} -4	D _{1,4} -8	D _{1,4} -8	D _{1,4} -9	D _{1,4} -9
Conditions of reactivation	1.0% Hydrazine	0.4% Hydrazine	0.3% Lithium aluminum hydride	0.5% Formaldehyde	0.3% Sodium borohydride	0.3% Glucose	0.5% Formaldehyde	0.7% Sodium tartrate	0.4% Hydrazine	2.0% Sodium formate
Temperature (°C)	60	20	20	20	20	20	20	20	20	20
Pressure (ata)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Time (hrs)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.									
Elimination percentage of poisonous materials (%)	12	41	43	43	43	52	44	44	45	45
Specific surface area (m ² /g-Ru)	89	91	93	93	93	97	90	88	92	90
Amount of catalyst required for reaction (ml)	34	36	36	36	34	40	36	36	36	36
	108	110	102	106	108	95	106	106	102	102

Example 22.

The reactivated catalysts obtained in Example 21 (Catalysts E_{1,6}-1, E_{1,6}-3 and E_{1,6}-5 to E_{1,6}-7) were each subjected to further treatment for reactivation under the conditions as described in Table 17. The thus reactivated catalysts were each reused 5 for continuous steam-reforming under the same conditions as shown in Example 15. The results are shown in Table 17.

As Table 17 shows, the catalysts (F_{1,7}-1 to F_{1,7}-5) reactivated in three steps are much recovered in catalytic activity.

TABLE 17

Catalyst		F ₁₇₋₁	F ₁₇₋₂	F ₁₇₋₃	F ₁₇₋₄	F ₁₇₋₅
Catalyst used		E ₁₆₋₁	E ₁₆₋₃	E ₁₆₋₅	E ₁₆₋₆	E ₁₆₋₇
Conditions of treatment for reactivation	Reactivating agent*)	H ₂	H ₂	H ₂ :H ₂ O (=1:1 by mol)	H ₂ O:N ₂ (=3:1 by mol)	O ₂ :H ₂ O:N ₂ (=10:50:40 by volume)
	Temperature (°C)	650	600	600	650	600
	Pressure (ata)	6.0	6.0	6.0	6.0	6.0
	Time (hrs)	12.0	6.0	6.0	12.0	10.0
	Post-treatment	—	—	—	—	—
Elimination percentage of poisonous materials (%)	Carbonaceous materials	100	86	87	100	100
	Sulfurous materials	96	96	96	97	94
Specific surface area (m ² /g-Ru)		35	37	35	40	37
Amount of catalyst required for reaction (ml)		100	96	102	93	98

Note: *) In case of Catalysts F₁₇₋₁ to F₁₇₋₅, the treatment was carried out with a space velocity of 2500 (l/hr).

Example 23.

The reactivated catalysts obtained in Example 20 (Catalysts E₁₅₋₁) and in Example 22 (Catalyst F₁₇₋₄) were each reused for steam-reforming under the same conditions as shown in Example 19. The results are shown in Table 18, from which it can be understood that the reactivated catalysts show the similar behavior to the fresh catalyst (Catalyst A₁₄) in depression of the catalytic activity, and that their catalytic activity, particularly that of Catalyst F₁₇₋₄, is nearly equal to the catalytic activity of the fresh catalyst.

TABLE 18

Catalyst		A ₁₄	E ₁₅₋₁	F ₁₇₋₄
Amount of catalyst required for reaction (ml)	Start	92	105	93
	600 hours	164	191	168
	1200 hours	221	260	227

Example 24.

A catalyst comprising 2% of ruthenium deposited on spheroidal particles of alumina of 4 mm in diameter (hereinafter referred to as "Catalyst A₁₈") (6700 ml) was charged into a tubular reactor of 5 inch in diameter, and methanol and steam were fed therein to effect a continuous steam-reforming reaction for 2000 hours under the following conditions:

Temperature of reactor: inlet, 580°C, outlet, 620°C;
 Space velocity: 15800 (l/hr);
 Ratio of steam/methanol: 1.5 (by mol);
 Pressure: 6 atm. (absolute)

After 2000 hours, the catalyst (hereinafter referred to as "Catalyst B₁₈") was treated under the same conditions as shown in Table 18 for reactivation. The reactivated catalyst was reused in steam-reforming reaction under the same conditions as mentioned above. The results are shown in Table 18.

5 As Table 18 shows, treatment with an inorganic alkaline substance or a reducing substance produces recovery of the catalytic activity.

TABLE 18

Catalyst	A ₁₈	B ₁₈	Reactivated			
			D ₁₈ -1	D ₁₈ -2	D ₁₈ -3	D ₁₈ -4
Conditions of reactivation						
Reactivating agent	-	-	0.375N NaOH	0.375N NaOH	1.0% Hydrazine	0.3% Glucose
Temperature (°C)	-	-	30	100	60	20
Pressure (ata)	-	-	1.0	1.0	1.0	1.0
Time (hrs)	-	-	3.0	3.0	3.0	3.0
Post-treatment	-	-	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.
Elimination percentage of poisonous materials (%)						
Carbonaceous materials	-	-	12	53	0	0
Sulfurous materials	-	-	-	-	-	-
Specific surface area (m ² /g-Ru)	43	17	20	34	23	23
Amount of catalyst required for reaction (ml)	1.3	-	-	1.6	3.8	4.0

Example 25.

The reactivated catalysts obtained in Example 24 (Catalysts D₁₈-1 to D₁₈-4) were each subjected to further treatment for reactivation under the conditions as shown in Table 19. The thus reactivated catalysts were each reused for continuous steam-reforming under the same conditions as described in Example 24. The results are shown in Table 19.

As Table 19 shows, the catalysts (E₁₉-1 to E₁₉-4) reactivated in two steps have recovered catalytic activity to a much greater extent than the catalysts (D₁₈-1 to D₁₈-4) reactivated in one step.

TABLE 19

Catalyst		E ₁₉ -1	E ₁₉ -2	E ₁₉ -3	E ₁₉ -4
Catalyst used		D ₁₈ -1	D ₁₈ -2	D ₁₈ -3	D ₁₈ -4
Conditions of treatment for reactivation	Reactivating agent	1.0% Hydrazine	0.3% Sodium borohydride	0.375N NaOH	0.375N NaOH
	Temperature (°C)	60	20	100	80
	Pressure (ata)	1.0	1.0	1.0	1.0
	Time (hrs)	3.0	3.0	3.0	3.0
	Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.		Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	
Elimination percentage of poisonous materials (%)	Carbonaceous materials	12	52	52	50
	Sulfurous materials	—	—	—	—
Specific surface area (m ² /g-Ru)		34	40	41	38
Amount of catalyst required for reaction (ml)		1.5	1.4	1.3	1.4

Example 26.

A catalyst comprising 2.0% of ruthenium deposited on spheroidal particles of alumina of 4 mm in diameter as a carrier material (hereinafter referred to as "Catalyst A₂₀") (290 ml) was charged into a tubular reactor of 1 inch in diameter, and methane and air were fed therein to effect continuously partial oxidation for 2500 hours under the following conditions:

Temperature of reactor: inlet, 310°C, outlet, 700°C;

Space velocity: 17500 (l/hr);

Ratio of air/methane: 2.37 (by mol);

Pressure: 1 atm. (absolute)

After 2500 hours, the resultant catalyst (hereinafter referred to as "Catalyst B₂₀") was treated under the conditions as shown in Table 20 for reactivation. The reactivated catalyst was reused in partial oxidation under the same conditions as mentioned above. The results are shown in Table 20.

As Table 20 indicates, treatment with an inorganic alkaline substance or a reducing substance shows recovery of the catalytic activity.

TABLE 20

Catalyst		A ₂₀	B ₂₀	Reactivated			
Conditions of treatment for reactivation	D ₂₀₋₁			D ₂₀₋₂	D ₂₀₋₃	D ₂₀₋₄	
Reactivating agent		—	—	0.375N NaOH	0.375N NaOH	1.0% Formaldehyde	2.0% Sodium formate
Temperature (°C)		—	—	30	100	60	20
Pressure (ata)		—	—	1.0	1.0	1.0	1.0
Time (hrs)		—	—	3.0	3.0	3.0	3.0
Post-treatment		—	—	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.	
Elimination percentage of poisonous materials (%)		—	—	12	52	0	0
Carbonaceous materials		—	—				
Sulfurous materials		—	—	32	95	70	55
Specific surface area (m ² /g-Ru)		43	17	21	33	21	21
Amount of catalyst required for reaction (ml)		58	—	—	67	170	172

Example 27.

The reactivated catalysts obtained in Example 26 (Catalysts D₁₀₋₁ to D₂₀₋₄) were each subjected to further treatment for reactivation under the conditions as shown in Table 21. The thus reactivated catalysts were each reused for continuous partial oxidation under the same conditions as shown in Example 26. The results are shown in Table 21.

Table 21 shows that, the catalysts (E₂₁-1 to E₂₁-4) reactivated in two steps recover catalytic activity to a much greater extent than the catalysts (D₂₀-1 to D₂₀-4) reactivated in one step.

TABLE 21

Catalyst		E ₂₁ -1	E ₂₁ -2	E ₂₁ -3	E ₂₁ -4
Catalyst used		D ₂₀ -1	D ₂₀ -1	D ₂₀ -3	D ₂₀ -4
Conditions of treatment for reactivation	Reactivating agent	1.0% Hydrazine	0.3% Sodium boro-hydride	0.375N NaOH	0.375N NaOH
	Temperature (°C)	60	20	80	80
	Pressure (ata)	1.0	1.0	1.0	1.0
	Time (hrs)	3.0	3.0	3.0	3.0
	Post-treatment	Water washing: 75°C, 3 hrs. Drying: 100°C, 16 hrs.		Water washing: 100°C, 2 hrs. Drying: 100°C, 16 hrs.	
Elimination percentage of poisonous materials (%)	Carbonaceous materials	12	52	47	47
	Sulfurous materials	95	97	92	93
Specific surface area (m ² /g-Ru)		34	40	39	37
Amount of catalyst required for reaction (ml)		68	62	60	62

WHAT WE CLAIM IS:—

1. A method for reactivation of a platinum group metal catalyst whose activity has been reduced as a result of its use to catalyse one of

(a) steam-reforming of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen,

(b) hydro-cracking of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen, and

(c) partial oxidation of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen to produce a combustible gaseous mixture usable as a fuel gas,

said method comprising the step of treating the platinum group metal catalyst of reduced catalytic activity in an aqueous medium with at least one inorganic alkali metal or alkaline earth metal compound and/or at least one reducing substance, so that the catalytic activity of the catalyst is at least partially recovered.

2. The method according to claim 1, wherein the treatment is carried out with at least one inorganic alkali metal or alkaline earth metal compound in an aqueous medium.

3. The method according to claim 2, wherein the treatment is carried out generally within the temperature range from 5 to 250°C.

4. The method according to claim 2 or claim 3 wherein the or each said inorganic compound is a hydroxide, carbonate, nitrate or sulfate of sodium, potassium, calcium, magnesium, barium or strontium.

5. The method according to any one of claims 2 to 4 wherein the concentration of said inorganic compound is in the range 0.001 to 10 N.

6. The method according to any one of claims 2 to 5 which further comprises the step of treating the platinum group metal catalyst with at least one reducing substance in an aqueous medium before or after the step of treating with said inorganic compound.

5 7. The method according to claim 6 wherein the or each reducing substance is hydrazine, formaldehyde, sodium borohydride, lithium aluminium hydride, sodium tartrate, potassium tartrate, sodium potassium tartrate, calcium tartrate, sodium hydrogen tartrate, sodium formate, potassium formate, calcium formate or glucose. 5

10 8. The method according to any one of claims 2 to 5, which further comprises the step of treating the platinum group metal catalyst with at least one of hydrogen, oxygen and steam before or after the step of treating with the inorganic compound. 10

15 9. The method according to claim 6 or claim 7, which further comprises the step of treating the platinum group metal catalyst with at least one of hydrogen, oxygen and steam before or after the step of treating with the inorganic compound or the step of treating with the reducing substance. 15

10. The method according to claim 1, wherein the treatment is carried out with at least one reducing substance in an aqueous medium.

11. The method according to claim 10, wherein the treatment is carried out generally within the temperature range 5 to 250°C.

20 12. The method according to claim 10 or claim 11, wherein the or each reducing substance is hydrazine, formaldehyde, sodium borohydride, lithium aluminium hydride, sodium tartrate, potassium tartrate, sodium potassium tartrate, calcium tartrate, sodium hydrogen tartrate, sodium formate, potassium formate, calcium formate or glucose. 20

25 13. The method according to claims 10 to 12, wherein the concentration of the reducing substance is from 0.01 to 10% by weight. 25

14. The method according to any one of claims 10 to 13, which comprises the step of treating the platinum group metal catalyst with at least one of hydrogen, oxygen, and steam before or after the step of treating with the reducing substance.

30 15. The method according to any one of the preceding claims, wherein the reactivation of the platinum group metal catalyst is achieved together with elimination of sulfurous materials deposited on the catalyst. 30

16. A method for elimination of sulfurous materials deposited on a platinum group metal catalyst as a result of its use to catalyse one of

35 (a) steam-reforming of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen, 35

(b) hydro-cracking of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen, and

40 (c) partial oxidation of one or more organic compounds consisting of carbon and hydrogen or of carbon, hydrogen and oxygen to produce a combustible gaseous mixture usable as a fuel gas, 40

said method comprising the step of treating the platinum group metal catalyst in an aqueous medium with at least one inorganic alkali metal or alkaline earth compound and/or at least one reducing substance, so that at least part of said sulfurous materials are eliminated.

45 17. A method according to claim 1 or claim 16 substantially as any herein described in the Examples. 45

18. A platinum group metal catalyst which has been treated by a method according to any one of the preceding claims.

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