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62/2520/01

RECOVERY METHOD OF RHODIUM

5 The present invention relates to a method for recovery of rhodium from an organic solution containing a rhodium complex having at least one type of organophosphorous compound as a ligand and an organophosphorous compound.

10 Recently, several methods have been developed wherein soluble complexes of rhodium and organophosphorous compounds are used as catalysts in a homogenous catalytic reaction. These complexes are useful for various reactions such as hydrogenation of olefins, carbonyl compounds and aromatic compounds, etc., hydroformylation and hydrocarboxylation of olefins. Also, since aforesaid
15 complexes are chemically very stable, the catalyst solution can be recycled in the reaction system after separating it from the reaction products by distillation.

20 However, since various high boiling by-products are formed in the aforesaid reaction and also the catalyst used in the reaction is partially inactivated, a part of the catalyst-containing residue obtained at the recovery of the reaction products by distillation must be removed continuously or intermittently to prevent the accumulation of high boiling by-products and the inactivated catalyst in
25 the reaction medium.

The catalyst-containing residue contains an expensive Group VIII noble metal and hence it is necessary to recover the noble metal efficiently.

30 Generally, to recover the noble metals a wet type recovery method can be used, in which sulfides are added to an organic solution containing noble metals such as rhodium, to form sulfides of the noble metals which are then recovered by precipitation. As an alternative method, noble metal compounds are reduced to metal by addition of
35 a reducing agent. As another alternative, the noble metals are adsorbed to an adsorbent such as an activated carbon.

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In still another method, the dry-type recovery method, an organic solution containing noble metals is combusted by using a combustion furnace or in-water combustion furnace to form ash from which rhodium can be recovered.

5 However, when using the conventional wet-type recovery method, it is not easy for rhodium complex with organophosphorous compounds to react with the sulfides or reducing agent; this is because the organophosphorous compounds are strongly bonded chemically with the noble
10 metal and the rhodium complexes are stable. And, the rhodium compounds are not absorbed sufficiently onto the activated carbon. It thus becomes a practical problem to recovery rhodium efficiently and effectively. Moreover, the waste chemicals and exhausted water need to be properly
15 treated as well. And the content of recovered noble metals is relatively low. These are technical drawbacks associated with the conventional wet-type recovery methods.

On the other hand, there are also drawbacks in the dry-type recovery method. The combustion using furnace
20 loses apportion of rhodium, and the obtained ash has a lot of impurities. Even if an in-water combustion furnace which demonstrates relatively high efficiency is employed, a portion of rhodium will be splashed and vaporised during the combustion process, and another portion of the rhodium
25 will be dissolved in the combustion liquid (namely, phosphorous aqueous solution), resulting in a low recovery percentage.

It is, therefore, an object of the present invention to overcome the aforementioned problems associated with
30 conventional methods for recovering noble metal, particularly rhodium. Namely an object of this invention is to provide a noble method for recovering rhodium as ash with high content from an organic solution containing a rhodium complex and organophosphorous compound.

35 As a result of continuous and diligent efforts to achieve the aforementioned objects, the present inventors have invented a novel method for the recovery of rhodium.



In it, an organic solution containing a rhodium complex having at least one type of organophosphorous compound as a ligand, together with an organophosphorous compound is ash-fired to obtain ash, and basic compound is added prior
5 to combustion in order to improve the recovery percentage of rhodium. Moreover, by controlling the ash-firing temperature so that it is lower than 1,000°C, rhodium can be recovered with higher efficiency. Furthermore, by cleaning with a cleaning solution containing a reducing
10 agent, recovery of rhodium as ash with high content can be achieved without loss of rhodium.

According to the present invention, a basic compound is added to an organic solution containing an organophorous compound and a rhodium complex having at least one type of
15 organophosphorous compound as a ligand, the solution is then combusted and ash-fired under a controlled temperature of less than 1,000°C, the ash is cleaned using a cleaning solution containing a reducing agent to remove soluble salts of elements other than rhodium. By the process
20 rhodium can be recovered at a high efficiency and in high yield and concentration.

As the method of the present invention may be used to recover rhodium from organic solution containing an organophosphorous compound and a rhodium complex having at
25 least one type of organophosphorous compound as a ligand, it can also be effectively applied to recover rhodium from a catalyst solution which has been separated, by distillation, from the reaction products of certain types of reactions, such as hydroformylation or
30 hydrocarboxylation using a homogeneous catalyst containing the rhodium complex and organophosphorous compound.

The rhodium complex containing at least one type of organophosphorous compound as a ligand can easily be prepared by the known prior art method from a rhodium
35 compound, such as a hydride, a halide, a carboxylate, a nitrate or a sulfrate of rhodium and an organophosphorous compound, such as a tertiary phosphine or phosphite. As



the case may be, also, the complex catalyst can be formed during the reaction by supplying a rhodium compound and an organophosphorous compound to the reactor.

Specific examples of rhodium compound which can be used in the preparation of Rh/organophosphorous complex are rhodium compound such as chloropentaaminorhodium (III) chloride, rhodium nitrate, rhodium trichloride, rhodium dicarbonylchloride, rhodium acetate, rhodium sulfate, etc.

Also, examples of the organophosphorous compound which can be used in the preparation of Rh/organophosphorous complex are phosphines such as tributylphosphine, chlorodiethylphosphine, tris-(aminoamyl)phosphine, tricyclohexylphosphine, triphenylphosphine, tri(N,N-dimethylanilino)phosphine, tris(o-tolyl)phosphine, phenyldiisopropylphosphine, pheneyldiamylphosphine, ethyldiphenylphosphine, chlorodihexylphosphine, tris(N,N-diethylaminomethyl) phosphine, ethylene-bis(diphenylphosphine), trianilinophosphine, dipheyl(N,N-d i m e t h y l a n i l i n o p h o s p h i n e) , triphenylanilinoethylenediphosphine, tris(3,5-diaminophenyl) phosphine, aminoethyltriisoprophylhexamethylenediphosphine, etc. phosphites such as trimethyl phosphite, triphenyl phosphite, chlorodiphenyl phosphite, tricyclophexyl phosphite, tetraphenylethylene diphosphite, etc.

According to the present invention, a basic compound is added prior to combusting an organic solution containing a rhodium complex and an organophosphorous compound as described above. the basic compound can be at least one of the group consisting of oxides, peroxides, hydroxides, and carbonates of group Ia or IIa elements in the periodic table; for example sodium oxide, sodium peroxide, caustic soda, pottassium hydroxide, sodium carbonate, potassium carbonate, sodium bicarbonate, magnesium oxide, calcium oxie, magnesium hydroxide, calcium hydroxide, magnesium carbonate or calcium carbonate. Alternative basic compounds which may be used include sulfides or hydrides of



group Ia elements in the period table; for instance, sodium sulfide, sodium borohydride or salts produced by combining alkali and organic acids; for example sodium formate, sodium acetate, sodium oxalate or sodium citrate.

5 Preferably the basic compounds are hydroxides or carbonates of group Ia elements in the periodic table, or salts produced by alkali and carboxylic acid; for example caustic soda, sodium formate or a mixture of caustic soda and other type of basic compounds such as sodium formate.

10 Although it is preferable to add these basic compounds as powder or granular shaped crystals to the organic solution, it is also possible to add them as either a solution or suspension. Moreover, the amount of added basic compounds, depending upon the amount of
15 organophosphorous compounds contained in in the organic solution, should be more than 0.1 molar equivalent to phosphorus atoms. The preferable range is from 0.1 to 20 equivalents. The most favourable range is from 0.3 to 10 equivalents. For an amount of less than 0.1 equivalent the
20 expected benefit according to this invention can not be achieved. On the other hand, at molar equivalencies over the excess amount, the rhodium recovery rate would not be improved, and the amount of ash formed in the combustion reaction will increase; thus the use of excess amount of
25 basic compounds is not practical.

Although it is normal practice to add the basic compounds to the organic solution before the combustion reaction, it is possible to add the basic compounds to the organic solution during the combustion reaction. In the
30 case where the combustion reaction is performed by spray combustion, the spray combustion can be accomplished by spraying the basic compound solution or suspension into the organic solution mist.

When combusting the organic solution containing a
35 rhodium complex and organophosphorous compounds to ash according to the present invention, the evaporating and the ashing temperature of the organic solution should be



controlled so as to improve the percentage of rhodium recovery. There are several methods for controlling the aforesaid temperature at a constant supply amount of the organic solution. For example these methods are
5 controlling the amount of air to be supplied for combustion, controlling temperature by water- or air-cooling, mixing non-flammable substance such as water in the organic solution, mixing an inert gas such as nitrogen in the supplied air, or combining the aforementioned
10 methods. Although the evaporation and ashing temperature can be controlled by any one of these methods, the most effective and economical way to control these temperatures is by controlling the amount of air supplied to the combustion reaction.

15 It is appropriate to control the evaporating temperature of the organic solution so that it is in a range of from 140 to 400°C during the combustion reaction. It is preferable to maintain this temperature in a range of from 160 to 350°C. For the evaporating temperature of
20 lower than 140°C, the combustion reaction would be unstable; more rhodium will be lost due to evaporation or splashing if the temperature is higher than 400°C.

It is appropriate to maintain the ashing temperature pan at higher than 500°C but lower than 1,000°C during the
25 combustion reaction; preferably it should be in a range of between 600 and 950°C. If it is lower than 500°C, it would be difficult to perform a complete ashing, while if it is higher than 1,000°C, more rhodium will be splashed or evaporated, resulting in a poor recovery percentage of
30 rhodium.

The combination of the aforementioned temperature control and the addition of the basic compounds improve the recovery of rhodium effectively in the process of evaporation and ashing of the organic solution.

35 Since large amounts of soluble impurities such as phosphoric acid or phosphoric salts are present in the fired and recovered ash of an organic solution containing



a rhodium complex and an organophosphorous compound, it is desirable to remove these impurities. In the present invention, soluble impurities are dissolved by cleaning the recovered ash, under retardation of elution of rhodium, and the ash containing rhodium is separated and recovered as the insoluble residue, so that rhodium can be recovered with higher efficiency. Water containing a reducing agent would be suitable as a cleaning solution. Although it is not necessary to heat the cleaning solution, the use of solution at a temperature more than 10°C increases the solubility of the impurities and thus improves the recovery rate of rhodium. The temperature of cleaning solution is preferably in the range of from 40 to 100°C; in the most preferable case, the cleaning solution is warm at the temperature of between 50 and 80°C.

Examples of possible reducing agents are formic acid, oxalic acid, hydrazine, or sodium borohydride. Sodium borohydride is the preferred reducing agent. The amount of the added reducing agent, depending on the presence or absence of the basic compound during the combustion reaction and the kind of the reducing agent, will be preferably in the range of from 0.001 mol/l to 0.5 mol/l; in the more preferable case, in the range of from 0.005 mol/l to 0.1 mol/l.

If less than 0.001 mol/l is added, the expected benefit of this invention can not be realised. On the other hand, if more than 0.5 mol/l is added the elution loss of rhodium will be constant and only the operation cost will increase, which is an undesirable result.

It is preferable to add the reducing agent prior to cleaning the ash, but it can also be added after putting the ash into the cleaning solution. A flocculant can aggregate the fine grained (smaller than 0,1 μm) type insoluble residue containing rhodium, so it is beneficial for the control of the loss of rhodium by controlling the filter leakage if during solid/liquid separation, especially the filtration operation after cleaning. And



this can control the loss of rhodium and enhance the filtration speed. As the type of the flocculant is not specifically limited as long as it is effective in aggregating the fine grained type residue in particular, it is appropriate to use a small amount of an effective polymeric flocculant and anionic or cationic polymer flocculant is preferred. When a polymeric flocculant is used, its quantity is decided in such a way that an aqueous solution prepared with a concentration of 0.01-0.05 wt% can be added to the cleaning solution until a flock is formed. Preferred quantities of the aforementioned aqueous solution containing flocculant are in the range of about 0.5-5 cc per 1 l cleaning solution. Although the flock can be formed even if excess solution is added, this is not preferable, since the filtration speed will be reduced.

The amount of cleaning solution needed must be 3-20 times more than the ash weight and an amount of 5-15 times more than the ash weight is preferable.

After introduction of the cleaning solution to the ash, the soluble salts will be dissolved in more than 10 minutes. The dissolving time can be effectively shortened by stirring the solution. Thereafter the insoluble residue containing rhodium is recovered by an ordinary filtration operation.

A single cleaning procedure enhances the rhodium content of ash, but the cleaning operation can also be repeated. When the cleaning is repeated, the additional cleaning can be done by the decantation method, not by the filtration operation. Moreover, if the filtered insoluble residue is ash-fired at 600-800°C for from 3 to 5 hours, followed by cleaning once at least as described above, the cleaning effect will be much improved.

As described above, in recovering rhodium from an organic solution containing a rhodium complex having at least one type of organophosphorous compound as a ligand and organophosphorous compound, any of the techniques of 1) adding the basic compound to an organic solution, 2)



controlling the evaporation and ashing temperature during the combustion reaction, and 3) using a cleaning solution containing reducing agent are individually effective; if two or three of these techniques are combined, the results are even better.

The invention is explained more specifically by reference to the following.

Example 1

An organic solution containing spent catalyst resulting from the hydroformylation of olefin with a rhodium triphenylphosphine complex, triphenylphosphine, triphenylphosphineoxide and high boiling by-products was used. A sample 20.00 g of organic solution containing 9.42 mg of rhodium (as calculated as a rhodium atom) and 0.72 g of phosphorus (as calculated as a phosphorus atom) was placed in a 60 ml alumina crucible. A 0.25 g (which is 0.27 equivalent to phosphorus) of granular caustic soda (NaOH) was added. After the generated vapour was ignited with heating the crucible up to 150-300°C by using a gas burner, the combustion was continued by blowing air into the crucible for about 10 minutes until the flame disappeared. The ash was collected and was burned further in an electric furnace at 800°C for 1 hour to obtain 0.72 g of ash. The ashing percentage was 2.6%. Rhodium contained in the ash was dissolved in potassium pyrosulfite. Result of absorptionmetry indicates that 8.57 mg of rhodium was obtained. the calculated percentage of rhodium recovered was 90.98%.

Example 2

Rhodium was recovered by procedures similar to those of Example 1, except that the amount of caustic soda added was changed to 0.35 g (which was 0.38 equivalent to phosphorus). The ashing percentage was 3.5% and 8.97 mg of rhodium was recovered. The recovered percentage of rhodium was 95.22%.



Example 3

Procedures similar to those of Example 1 were performed except that the amount of caustic soda added was changed to 0.5 g (which was 0.54 equivalent to phosphorus).
5 The ashing percentage was 4.8% and 9.16 mg of rhodium was obtained. The recovered percentage of rhodium was 97.24%.

Example 4

Rhodium was recovered by procedures similar to Example 1 except that the amount of caustic soda added was changed
10 to 0.75 g (which was 0.81 equivalent to phosphorus). The ashing percentage was 5.9% and 9.41 mg of rhodium was recovered. The percentage of rhodium recovered was 99.89%.

Example 5

Adding 1.0 g of caustic soda (which was 1.08
15 equivalent to phosphorus), procedures similar to those of Example 1 were performed. The ashing percentage was 7.3% and 9.32 mg of rhodium was collected. The recovered percentage of rhodium was 98.94%.

Example 6

Similar procedures were carried out to recover rhodium
20 as in Example 1 except that the added amount of caustic soda was changed to 1.5 g (which was 1.62 equivalent to phosphorus). The ashing percentage was 9.7% and 9.31 mg of rhodium was recovered. The recovery percentage of rhodium
25 was 98.83%.

Example 7

Except that the added amount of the caustic soda was changed to 4.0 g (which was 4.31 equivalent to phosphorus), similar procedures were performed to recover rhodium as in
30 Example 1. The ashing percentage was 26.6% and 9.40 mg of rhodium was recovered. The recovery percentage was 99.79%.

Example 8

Instead of granular caustic soda, potassium carbonate (K_2CO_3) 2.0 g (which was 1.22 equivalent to phosphorus) was
35 added. The rest of procedures was similar to those employed for Example 1. Rhodium in the amount of 9.09 mg was obtained. The recovery percentage was 96.50%.



Example 9

Similar procedures to those of Example 1 were performed to recover rhodium, except that instead of granular caustic soda, 3.0 g (which was 1.06 equivalent to phosphorus) of powder sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) was utilised. Rhodium in the amount of 8.98 mg was recovered. The recovery percentage was 95.33%.

Example 10

Instead of granular caustic soda, 25 wt.% caustic soda aqueous solution of 2.0 g (which was 0.54 equivalent to phosphorus) was added. The procedures used were the same as for Example 1. Rhodium in the amount of 9.18 mg was recovered. The recovery percentage was 97.45%.

Example 11

A 40 wt.% potassium carbonate aqueous solution 4.2 g (which was 1.05 equivalent to phosphorus) was used instead of granular caustic soda, in procedures otherwise the same as those performed to in Example 1. A recovery of 9.11 mg was obtained. The recovery percentage was 96.71%.

Example 12

Instead of caustic soda, a mixture of 40 wt.% potassium carbonate (1.4 g) and 1.2 wt.% sodium borohydride (SBH) (2.0 g), for a total of 0.46 equivalent to phosphorus) was added. Procedures used were similar to those of Example 1. Rhodium in the amount of 9.14 mg was recovered. The recovery percentage was 97.03%.

Example 13

Procedures similar to those of the Example 1 were performed, except that 1.0 g of powdered calcium hydroxide (which was 1.16 equivalent to phosphorus) was used, resulting in a yield of 8.80 mg of rhodium. The recovery percentage was 93.42%.

Example 14

Except that 12 wt.% SBH (1.5 g which was 0.87 equivalent to phosphorus) was used instead of caustic soda, procedures similar to those of Example 1 were used.



Rhodium in the amount of 9.03 mg was collected. The recovery percentage was 95.86%.

Example 15

5 Instead of granular caustic soda, 0.8 g of powdered sodium formate (NaHCOO) (which was 0.50 equivalent to phosphorus) was used, in procedures similar to those of Example 1. Rhodium in the amount of 8.82 mg was recovered. The recovery percentage was 93.63%.

Example 16

10 Procedure similar to those of Example 1 was employed to recover rhodium, except that 1.1 g of powdered sodium formate (which was 0.69 equivalent to phosphorus) was used. Rhodium in the amount of 9.39 mg was recovered. The recovery percentage was 99.68%.

15 Example 17

Instead of granular caustic soda, 0.4 g of powdered sodium formate and 0.4 g of granular caustic soda (total molar equivalent of 0.68 to phosphorus) was added. The remaining procedures were similar to those of Example 1. Rhodium in the amount of 9.27 mg was recovered. The recovery percentage was 98.14%.

Comparative Example 1

As in Example 1, 20.00 g of organic solution was measured into a 60 cc alumina crucible. However, granular caustic soda was not added. Rhodium recovery was 7.80 mg. The recovery percentage was 82.80%.

Comparative Example 2

30 Similar procedures were performed as in Example 1, except that 1.5 g of sodium chloride (NaCl , which was 1.10 equivalent to phosphorus) was used to recover rhodium. Recovery of 7.87 mg of rhodium was obtained. The recovery percentage was 83.55%.

As clearly shown in the aforementioned examples and comparative examples, rhodium was recovered at a recovery percentage of greater than 90%; this compares with rhodium recovery of only about 80% using prior art methods.

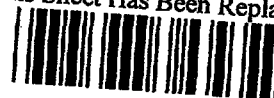


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Data on the amount of added basic compounds, molar equivalency to phosphorus, and the recovery percentage of rhodium are listed in Tables 1 and 2.

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TABLE 1

Example	Type of Basic Compounds	Amount Added (g)	Equiv. to phosphorus	Rhodium Recovery Amount (mg)	Rhodium Recovery Percent (%)	
5	1	GRANULAR NaOH	0.25	0.27	8.57	90.98
	2	GRANULAR NaOH	0.35	0.38	8.97	95.22
	3	GRANULAR NaOH	0.5	0.54	9.16	97.24
10	4	GRANULAR NaOH	0.75	0.81	9.41	99.89
	5	GRANULAR NaOH	1.0	1.08	9.32	98.94
	6	GRANULAR NaOH	1.5	1.62	9.31	98.83
15	7	GRANULAR NaOH	4.0	4.31	9.40	99.79
	8	POWDERED K ₂ CO ₃	2.0	1.22	9.09	96.50
	9	POWDERED Na ₂ S.9H ₂ O	3.0	1.06	8.98	95.33
20	10	25 wt % NaOH sol'n	2.0	0.54	9.18	97.45
	11	40 wt % K ₂ CO ₃ sol'n	4.2	1.05	9.11	96.71
	12	40 wt % K ₂ CO ₃ sol'n + 1.2 wt % SBH	1.4 2.0	0.46	9.14	97.03
25	13	POWDERED Ca(OH) ₂	1.0	1.16	8.80	93.42
	14	12 wt % SBH	1.5	0.87	9.03	95.86
	15	POWDERED NaHCOO	0.8	0.50	8.82	93.63
	16	POWDERED NaHCOO	1.1	0.69	9.39	99.68
	17	POWDERED NaHCOO + GRANULAR NaOH	0.4 0.4	0.68	9.27	98.41

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TABLE 2

COMPARA-TIVE EXAMPLE	TYPE OF ADDITIVE	AMOUNT ADDED (g)	EQUIVALENT TO PHOSPHORUS	RHODIUM RECOVERY AMOUNT (mg)	RHODIUM RECOVERY PERCENT (%)
1	-	-	-	7.80	82.80
2	NaCl	1.5	1.10	7.87	83.55

As seen from the results of Examples 1 through 17 and comparative example 1 and 2, when combustng and ash-firing an organic solution containing rhodium complex having at least one type of organophosphorous compound as a ligand and organophosphorous compound to recover rhodium, it was found that the recovery percentage of rhodium was significantly improved by adding basic compounds to said organic solution. The procedure used was easily performed.

Example 18

An organic solution containing spent catalyst resulting from the hydroformylation of olefins with rhodium-triphenylphosphine complex, triphenylphosphine, triphenylphosphineoxide and high boiling by-products, where 10.00 kg of organic solution contained 4.75 g of rhodium (as calculated as a rhodium atom) and 359 g of phosphorous (as calculated as a phosphorous atom) was examined. Four identical examples were prepared. A stainless steel combustion container with a 20 cm diameter and 10 cm depth was placed on the heater. Each sample was injected to the container with a flow rate of about 40-50 g/min by using a pump. The evaporating temperature was controlled by the amount of air blown into the heater and combustion container through a pipe with a 50 mm inner diameter from the blower, evaporation temperatures of 160-200°C, 200-250°C, 250-300°C and 300-350°C, were used, followed by ash-firing at at 700°C for 4 hours. A percentage of rhodium recovery corresponding to the evaporating temperature of the organic solution was obtained by analysis of rhodium in the fired ash. Results are shown in Table 3.



TABLE 3

BOILING TEMP. OF SOL'N (°C)	AMOUNT OF RHODIUM RECOVERED (%)	RHODIUM RECOVERY PERCENTAGE (%)
160-200	4.451	93.7
200-250	4.437	93.4
250-300	4.413	92.9
300-350	4.380	92.2

Example 19

Four samples were combusted under procedures similar to those of Example 18, except for the evaporating temperature and the ashing temperature. The evaporating temperature of the organic solution was maintained at 200-250°C, and the ash-firing temperature was 800°C, 850°C, 900°C, or 950°C for 4 hours. The recovery percentage of rhodium was obtained from the analysis of the rhodium content of the ashes. Results are shown in Table 4.

TABLE 4

ASHING TEMP (°C)	RHODIUM AMOUNT RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
800	4.432	93.3
850	4.431	93.3
900	4.375	92.1
950	4.372	92.0

Comparative Example 3

Except that the evaporation temperatures were controlled at 400-450°C, 450-500°C, and 500-600°C, procedures similar to those of Example 18 were performed. The recovery percentage of rhodium was obtained from the analysis of rhodium content in ash. The results are listed in Table 5.





TABLE 5

EVAPORATION TEMP. OF SOL'N (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
400-450	4.241	89.3
450-500	4.204	88.5
500-600	4.147	87.3

Comparative Example 4

Procedures similar to Example 19 were used except that an ash-firing temperature of 1,000°C, 1,100°C, or 1,200°C for 4 hours was used. The recovery percentages of rhodium are listed in Table 6.

TABLE 6

ASHING TEMP. (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
100	4.189	88.2
1100	4.166	87.7
1200	4.114	86.6

Example 20

500 g of powdered sodium formate (NaHCOO which was 0.63 equivalent to phosphorous) was added to 10.00 kg of the organic solution. The remaining procedures were similar to those employed for Example 18. The recovery percentages of rhodium are presented in Table 7.

TABLE 7

EVAPORATION TEMP. OF SOL'N (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
160-200	4.745	99.9
200-250	4.741	99.8
250-300	4.693	98.8
300-350	4.679	98.5

Example 21

Except that 500 g of powdered sodium formate (NaHCOO which was 0.63 equivalent to phosphorous) was added to

10.00 kg of the organic solution, procedures similar to those of Example 19 were used. The percentage rhodium recovered was obtained from rhodium the analysis of rhodium content in ash. Results are listed in Table 8.

5

TABLE 8

ASHING TEMP. (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
800	4.736	99.7
850	4.726	99.5
900	4.724	99.5
950	4.712	99.2

10

Comparative Example 5

Procedures similar to Example 20 were used, except that the evaporation temperature was maintained at 400-450°C, 450-500°C. The percentage of rhodium recovered was obtained from the analysis of rhodium content in ash. Results are listed in Table 9.

15

TABLE 9

EVAPORATION TEMP. OF SOL'N (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
400-450	4.522	95.2
450-500	4.479	94.3
500-600	4.441	93.5

20

25 Comparative Example 6

The procedures similar to those of Example 21 were used except that the ash-firing temperature of 1,000°C, 1,100°C or 1,200°C for 4 hours was used. The percentage of rhodium recovered was obtained from the analysis of rhodium content in ash. Results are listed in Table 10.

30



TABLE 10

ASHING TEMP. (°C)	AMOUNT OF RHODIUM RECOVERED (g)	RHODIUM RECOVERY PERCENTAGE (%)
1000	4.484	94.4
1100	4.446	93.6
1200	4.422	93.1

From the above Example 18 through 21 the Comparative Example 3 through 6, in which the rhodium was recovered by combusting and ash-firing organic solutions containing rhodium complex having at least one type of organophosphorous compound as a ligand and organophosphorous compound, it was found that the recovery percentage of rhodium was significantly improved by controlling the evaporation temperature and ashing temperature during the combustion reaction with an easily performed procedure.

Example 22

An organic solution containing spent catalyst resulting from the hydroformylation reaction of olefins with rhodium-triphenylphosphine complex triphenylphosphine, triphenylphosphineoxide and high boiling by-product was prepared. Such an organic solution of 1,000 g contained 475 mg of rhodium (as calculated as a rhodium atom) and 35.9 g of phosphorus (as calculated as a phosphorus). Samples were placed in an AISI type 304 stainless steel combustion container with a capacity of 3.1ℓ (having 20 cm diameter and 10 cm depth) and the burner fired for about 30 minutes to produce ash. The evaporation temperature of the organic solution was maintained at 200-250°C, and the ashing temperature was maintained at 700-800°C. Furthermore, the un-combusted tar-like substance was burned at 650°C for 4 hours in the electric furnace. The recovery percentage at this step was 94-95%.

In the next step, a cleaning solution was prepared by mixing an original cleaning solution, which is a mixture of 1 ℓ of about 70°C warm water and sodium borohydride (SBH)



0.01 mol, together with 0.02 wt.% of aqueous solution of the polymeric flocculant aronflock (A-101; Toa-Gosei Chemical Co. Ltd.) 5 cc. After adding the ash and washing for about 30 minutes while stirring, the undissolved residues were filtered. The filtrate was combusted and ash-fired along with the filtration paper at 650°C for 4 hours (the second ashing). Except that the concentration of the sodium borohydride was maintained at 0.01, 0.05 and 0.1 mol/l, respectively, the ashing, cleaning and burning were performed on three other samples, using similar procedures as in the previous example. Rhodium content and elution loss of rhodium were obtained from analysis of the ash before and after the cleaning process and the cleaning solution. Results are tabulated in Table 11.

TABLE 11

CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
SBH		Rh CONTENT IN ASH	Rh CONTENT IN ASH	
mol/l	mol/l	wt %	wt %	%
0.01	2.43	0.59	12.12	3.01
0.05	12.15	0.60	13.32	0.64
0.1	24.29	0.60	13.25	0.57

Example 23

Using hydrazine hydrate instead of sodium borohydride (SBH) as a reducing agent, the amount used was 0.01, 0.05, 0.1, and 0.5 mol/l respectively in four experiments. An ashing, cleaning and burning were performed using procedures similar to those of Example 22. From analysis of the ash before and after the cleaning, and in the cleaning solution, rhodium content and cleaning, elution loss of rhodium was obtained. Results are listed in Table 12.



TABLE 12

CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
HYDRAZINE HYDRATE		Rh CONTENT IN ASH	Rh CONTENT IN ASH	
mol/l	mol/l	wt %	wt %	%
0.01	0.6	0.60	11.95	7.25
0.05	3.1	0.60	12.78	0.90
0.1	6.3	0.60	13.40	0.86
0.5	31.3	0.60	13.13	0.86

Comparative Example 7

Except that the reducing agent was not added procedures similar to Example 22 were carried out. Results are shown in Table 13.

TABLE 13

COMPARATIVE EXAMPLE	CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
			Rh CONTENT IN ASH	Rh CONTENT IN ASH	
No.	mol/l	mol/l	wt %	wt %	%
7	0	0	0.60	8.84	14.63

Example 24

The first combusting was done after adding the 50 g of sodium formate (which was 0.63 equivalent to phosphorous and the amount of sodium borohydride (SBH) added to the cleaning solution was changed to 0.001, 0.005, 0.01, 0.05, and 0.01 mol/l respectively in five experiments. The remaining procedures used were similar to those employed for Example 22. The recovery percentage for rhodium before cleaning was 99-9.8%. Results are seen in Table 14.



TABLE 14

	CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS OF % of Rh
	SBH		Rh CONTENT IN ASH	Rh CONTENT IN ASH	
5	mol/l	mol/l	wt %	wt %	%
	0.001	0.24	0.58	25.55	1.43
	0.005	1.21	0.58	28.39	0.63
	0.01	2.43	0.59	27.04	0.25
	0.05	12.15	0.58	27.23	0.10
10	0.1	24.29	0.58	27.55	0.10

Example 25

The reducing agent was changed from sodium borohydride (SBH) to hydrazine hydrate and the amount of hydrazine hydrate added was also changed to 0.005, 0.01, 0.05, 0.1 and 0.5 mol/l respectively in five experiments. The rest of procedures were similar to those used for Example 24. The results are listed in Table 15.

TABLE 15

	CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
	HYDRAZINE HYDRATE		Rh CONTENT IN ASH	Rh CONTENT IN ASH	
20	mol/l	mol/l	wt %	wt %	%
	0.005	0.3	0.58	25.88	1.25
25	0.01	0.6	0.59	26.90	0.75
	0.05	3.1	0.58	27.18	0.30
	0.1	6.3	0.58	27.49	0.30
	0.5	31.3	0.58	26.27	0.30

Example 26

The sodium borohydride (SBH) was added in the amount of 0.05 mol/l, and 1.73 mol of caustic soda was added to the cleaning solution. Otherwise procedures were similar



to those employed for Example 22. Results are listed in Table 16.

Example 27

5 Except that the sodium borohydride (SBH) was replaced by hydrazine hydrate for the cleaning operation, the same procedures were performed as in Example 26. Results are listed in Table 16.

TABLE 16

EXAMPLE	BASIC COMPOUNDS	BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
	NaOH	Rh CONTENT IN ASH	Rh CONTENT IN ASH	
No.	mol/l	wt %	wt %	%
26	1.73	0.59	9.19	0.33
27	1.73	0.60	9.95	0.54

Example 28

15 Ash which was obtained through the procedures of Example 24 was further subjected to a second cleaning using a celaning solution which was a mixture of 0.001 mol/l of sodium borohydride (SBH) and 1.0 l of 70°C warm water and 5 ml of 0.02% by weight of aqueous solution of the
20 polymeric flocculant Aronflock. This was followed by a second burning.

Example 29

Changing the amount of sodium borohydride (SBH) used



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for the second cleaning to 0.005 mol/l, the remaining procedures were similar to those used for Example 28. Results of Example 28 and 29 are listed in Table 17.

TABLE 17

5

10

EXAMPLE	CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
	SBH		Rh CONTENT IN ASH	Rh CONTENT IN ASH	
No.	mol/l	mol/l	wt %	wt %	%
28	0.001	0.24	0.63	67.33	1.73
29	0.005	1.21	0.63	51.97	0.82

15

Comparative example 8

Except that the reducing agent was not added the rest of the procedures were similar to those employed for Example 24. Results are listed in Table 18.

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TABLE-18

COMPARATIVE EXAMPLE	CONCENTRATION OF REDUCING AGENT		BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS % OF Rh
	mcl/l	mol/l	Rh CONTENT IN ASH	Rh CONTENT IN ASH	
8	0	0	0.58	22.83	4.21

[Comparative example 9]

Procedures (namely, the ashing, cleaning, and burning) were used as in Example 26 except the reducing agent was not added. The results are presented in Table 19.

TABLE 19

COMPARATIVE EXAMPLE	BASIC COMPOUND	BEFORE THE CLEANING	AFTER THE CLEANING	ELUTION LOSS OF % OF Rh
	NaOH	Rh CONTENT IN ASH	Rh CONTENT IN ASH	
No.	mol	wt %	wt %	%
3	1.73	0.60	8.90	6.45

As seen from above Example 22 through 29 and Comparative examples 7 and 8, after combusting the organic solution containing a rhodium complex having at least

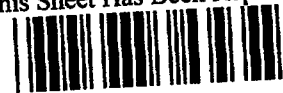


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one type of organophosphorous compound as a ligand and an
organophosphorous compound, the ash was further washed and
cleaned with a cleaning solution which was a mixture of a
reducing agent, flocculant and water to remove soluble
5 impurities without the loss of rhodium. Thus rhodium can
be recovered with high content and efficiency.

While this invention has been explained with reference
to the method described herein, it is not confined to the
details as set forth and this application is intended to
10 cover any modifications and changes as may come within the
scope of the following claims.

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CLAIMS

1. A method for recovering rhodium from a first organic solution comprising a) a rhodium complex containing organophosphorous ligand and b) an organophosphorous compound, comprising the steps of:
 - 5 adding a basic compound to said first solution producing a resultant organic solution, and
 - combusting said resultant organic solution to ash.
2. The method for recovering rhodium according to claim 1, wherein said basic composition comprises at least one basic compound selected from a group comprising oxides, peroxides, hydroxides and carbonates of group Ia and group IIa elements in the Periodic Table.
3. The method for recovering rhodium according to claim 1, wherein the basic compound comprises at least one basic compound selected from a group comprising sulfides and hydrides of the group Ia elements in the Periodic Table.
4. The method for recovering rhodium according to claim 1, wherein the basic compound comprises at least one of a group of salts produced by a reaction of alkali with organic acid.
5. The method for recovering rhodium as according to any preceding claim, wherein the basic compound is added in an amount of more than 0.1 molar equivalent but less than 20 molar equivalents to phosphorus atoms which are contained in the resulting organic solution.
6. The method for recovering rhodium according to any preceding claim, wherein the combustion temperature at which ash is formed is maintained at less than 1,000°C.
7. The method for recovering rhodium according to any preceding claim, comprising the further step of:
 - cleaning said ash by using a cleaning solution containing a reducing agent to remove impurities such as soluble salts of elements other than rhodium.
8. A method for recovering rhodium from a first organic solution comprising a) a rhodium complex containing an organophosphorous ligand and b) an organophosphorous

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compound, wherein said first organic solution is combusted to ash, the improvement comprising:

controlling the combustion temperature at which ash is formed to remain at less than 1,000°.

- 5 9. The method for recovering rhodium according to any preceding claim including the step of evaporating said organic solution prior to combustion to ash and the temperature during said evaporation step is maintained at less than 400°C
- 10 10. A method for recovering rhodium from a first organic solution comprising a) a rhodium complex containing an organophosphorous ligand and b) an organophosphorous compound, wherein said first organic solution is combusted to ash, the improvement comprising the further step of:
- 15 cleaning said ash by using a cleaning solution containing a reducing agent to remove impurities such as soluble salts of elements other than rhodium.
11. The method for recovering rhodium according to claim 10, wherein a basic compound is added to said cleaning
- 20 solution.
12. The method for recovering rhodium according to claim 10 or 11, wherein cleaning or cleaning followed by burning is performed more than twice.
13. The method for recovering rhodium according to any of
- 25 claims 10 to 12, wherein a flocculant is added to said cleaning solution.
14. The method according to any of claims 7 and 10 to 13 in which the reducing agent is selected from formic acid, oxalic acid, hydrazine, or sodium borohydride.
- 30 15. The method according to any of claims 7 and 10 to 14 in which the amount of reducing agent present is in the range 0.001 M to 0.5 M.
16. The method for recovering rhodium according to claim 10, wherein said cleaning solution comprises water or warm
- 35 water.
17. A method according to any preceding claim in which the first organic solution is derived from a catalyst solution





separated from a hydroformylation or hydrocarboxylation reaction.

18. A method according to any preceding claim in which the rhodium complex contains at least one phosphine ligand.