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PATENT SPECIFICATION

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(54) PROCESS FOR RECOVERING NOBLE METAL

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a Japanese Company, of No. 5—2, Marunouchi 2-Chome, Chiyoda-ku, Tokyo, 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:—

This invention relates to a process for recovering a Group VIII noble metal from a solution containing a complex of a Group VIII noble metal containing an organophosphorus compound as a ligand.

Recently, a process has been developed wherein a soluble complex of a Group VIII noble meal with an organophosphorus compound is used as a catalyst in a homogeneous catalytic reaction. The complex is useful for various reactions such as the hydrogenation of olefins, carbonyl compounds or aromatic compounds, and the hydroformylation of olefins, e.g., as disclosed in U.S. Patent Specification No. 2,527,809, and the hydrocarboxylation of olefins, e.g., as disclosed in Japanese Patent Publication No. 25050/1972. Also, since the aforesaid complex is chemically quite stable, the complex remains unchanged in the residue when recovering the reaction product by distilling a reaction mixture formed in the reaction in which the complex has been used as the catalyst. Consequently, the residue containing the complex can be recycled for re-use as a catalyst. However, since various high boiling by-products are formed in the aforesaid reaction and since also the catalyst used in the reaction is partially inactivated, some of the catalyst-containing residue obtained from recovery of the reaction product by distillation must be removed, either continuously or intermittently, in order to prevent the accumulation in the reaction medium of the high boiling by-products and the inactivated catalyst.

The catalyst-containing residue contains an expensive Group VIII noble metal and hence it is necessary to recover the noble metal efficiently: it is also necessary to convert the organophosphorus compound, which is contained in the residue in the free state or in combination with the noble metal, to an innocuous compound to protect the environment from pollution and it is also desirable on economic grounds to recover the organophosphorus compound as a utilisable compound.

Previously adsorption, extraction using a strong acid (as disclosed in U.S. Patent Specification No. 3,641,076) and decomposition by a peroxide have each been proposed as methods of recovering the noble metal catalyst. However, in such conventional processes the noble metal catalyst cannot be recovered in high yield since the organophosphorus compound present in the residue hinders the adsorption of the noble metal catalyst and furthermore the complex is too stable to be decomposed readily. Again, in the conventional processes described above, the phosphorus compound contained in the residue from which the noble metal catalyst has been recovered must be subjected to further treatment.

An object of this invention is, therefore, to provide a process for recovering a Group VIII noble metal from a solution containing a complex of the noble metal with an organophosphorus compound unattended by the aforesaid difficulties.

According to the present invention there is provided a process for recovering a noble metal of Group VIII of Mendeléeff's periodic table comprising burning in an oxygen-containing gas an organic solvent solution containing a soluble complex of a Group VIII noble metal which complex contains at least one organophosphorus compound as a ligand, immediately introducing the combustion product into an aqueous absorption liquid to retain therein particles of the Group VIII noble metal and the phosphorus oxide formed by the burning and recovering the noble metal particles from said aqueous liquid.

The solution remaining is an aqueous solution of phosphoric acid and it may be discharged into a drain after neutralization or can, if desired, be used for various purposes.

The process of this invention may be applied to the recovery of a Group VIII noble metal such as ruthenium, rhodium, palladium,

iridium or platinum from any organic solvent solution containing a complex of a Group VIII noble metal with an organophosphorus compound. While not desiring to be bound by any particular explanation, it is believed that the Group VIII noble metal forms a complex together with an organophosphorus compound or, as the case may be, with an organophosphorus compound and one or more other ligands such as carbonyl, nitrosyl, halogen, olefin, hydrogen and cyano groups. The process of this invention can be particularly usefully applied for recovering the Group VIII noble metal from a waste catalyst solution which results from the hydroformylation or carboxylation of olefins and contains a complex of the Group VIII noble metal compound with an organophosphorus compound. In this case, the waste catalyst solution usually contains reaction products and reaction solvent and thus it is advantageous to concentrate the waste solution containing the complex of the Group VIII noble metal by distilling off the reaction products and reaction solvent and then recovering the noble metal from the concentrate by the process of this invention. An example of a suitable organic solvent solution for the process of this invention is a residue of a reaction mixture obtained in the hydroformylation of an olefin using as a catalyst a soluble complex containing rhodium and a tertiary phosphine and from which the aldehyde formed has been removed by distillation.

The complex of the Group VIII noble metal containing an organophosphorus compound as a ligand can be easily prepared by a known complex-forming process from a compound of the Group VIII noble metal, such as hydroxide, a halide, a carboxylate, a nitrate or a sulphate, of the noble metal, and an organophosphorus compound, such as a tertiary phosphine or phosphite. The complex may also be formed during the reaction by supplying a compound of the Group VIII noble metal and an organophosphorus compound to the reactor.

Specific examples of the Group VIII noble metal compounds which may be used in the preparation of the noble metal/organophosphorus complex are a ruthenium compound such as ruthenium trichloride or tetraamino ruthenium hydroxychloride; a rhodium compound such as chloropentaaminorhodium (III) chloride, rhodium nitrate, rhodium trichloride, rhodium dicarbonylchloride, rhodium acetate or rhodium sulphate; a palladium compound such as palladium hydroxide, palladous chloride, palladous cyanide, palladous iodide, palladous nitrate, palladium cyanide, palladium acetate or palladium sulphate; an iridium compound such as iridium tribromide, iridium tetrabromide, iridium trifluoride, iridium trichloride or iridium carbonyl; and a platinum compound such as platinic acid, platinous iodide, sodium hexachloroplatinate or potassium trichloroethyleneplatinate.

Also, examples of the organophosphorus compound which may be used in the preparation of the noble metal/organophosphorus complex are a phosphine such as trimethylphosphine, chlorodiethylphosphine, tris(aminoamyl)phosphine, tricyclohexylphosphine, triphenylphosphine, tris(N,N-dimethylanilino)-phosphine, tris(*o* - tolyl)phosphine, phenyldiisopropylphosphine, phenyldiamylphosphine, ethyldiphenylphosphine, chlorodihexylphosphine, tris(N,N - diethylaminomethyl)phosphine, ethylene - bis(diphenylphosphine), trianilinophosphine, diphenyl(N,N - dimethylanilinophosphine), triphenylanilinoethylenediphosphine, tris(3,5 - diaminophenyl)phosphine, or aminoethyltriisopropylhexamethylenediphosphine; a phosphite such as trimethyl phosphite, triphenyl phosphite, chlorodiphenyl phosphite, tricyclohexyl phosphite or tetraphenylethylene diphosphite and a penta-valent organophosphorus compound such as triphenylphosphine oxide.

In the process of this invention, the Group VIII noble metal may be recovered from the solution containing the soluble complex of the Group VIII noble metal which contains the above-described Group VIII noble metal compound and the organophosphorus compound as a ligand and, if desired, may further contain free organophosphorus compound at various concentrations. However, generally the concentration of the noble metal in the organic solvent is preferably adjusted to from 0.05 to 2% by weight calculated as the metal, prior to supplying the above-described solution into the combustion zone. The concentration of the organophosphorus in the organic solvent is generally adjusted to from 0.1 to 5% by weight, preferably from 0.1 to 2% by weight, calculated as phosphorus.

Suitable organic solvents include an aromatic hydrocarbon containing from 6 to 8 carbon atoms such as benzene, toluene or xylene; a paraffinic hydrocarbon containing from 8 to 12 carbon atoms such as octane, decane and dodecane; an aliphatic alcohol containing from 2 to 8 carbon atoms such as butanol, pentanol, octanol or ethylene glycol; an aliphatic aldehyde containing from 4 to 8 carbon atoms such as butanal; an aliphatic or alicyclic ester containing from 4 to 8 carbon atoms such as butyl acetate or γ-butyrolactone; and a high boiling by-product resulting from the hydroformylation or hydrocarboxylation of an olefin wherein a soluble complex of a Group VIII noble metal and an organophosphorus compound is used as a catalyst.

Suitable methods which may be used for combustion of the above-described solution include burning the solution is a conventional furnace and introducing the combustion gas formed into an absorption liquid by aspirating

particles and at the same time the organophosphorus compound is recovered or discharged as innocuous phosphoric acid or phosphate.

The invention will now be illustrated by the following specific Examples.

EXAMPLE 1

Into a drum 1 of a submerged combustion device having an inside capacity of 0.5 m^3 and as shown in the drawing, there was charged 0.3 m^3 of water 2; and to the burner 4 there were supplied through the conduit 9 at a rate of 5 kg/hr a toluene solution containing tris(triphenylphosphine) rhodium carbonylhydride

$$(RhH(CO)[P(C_6H_5)_3]_3)$$

in an amount of 0.3% by weight, as metallic rhodium, triphenylphosphine and triphenylphosphine oxide in amounts of 3% and 2% by weight, respectively, and high boiling by-products resulting from the hydroformylation of propylene in an amount of 21.2% by weight, and through the conduit 10 air at a rate of 60 Nm^3/hr, and burned at about 1180°C. The combustion product was immediately introduced into the water 2 and its residence time in the combustion chamber was 0.5 second. Phosphorus oxide formed in the combustion was absorbed by the water 2 to provide phosphoric acid and the rhodium formed was dispersed in the water 2 as solid particles.

While supplying water through conduit 14 so that the volume of water 2 in the absorption drum 1 was always maintained at 0.3 m^3, combustion was conducted continuously for 20 hours and then the combustion products in the combustion device were filtered, whereby there were recovered 95% of the rhodium as solid particles, and almost 100% of the phosphorus, as phosphoric acid.

EXAMPLE 2

A xylene solution containing a rhodium complex which contains triphenylphosphite as a ligand, in an amount of 0.3% by weight, as metallic rhodium and free triphenylphosphite and oxide of triphenylphosphite in an amount of 3.0% and 2.0% by weight, respectively, and high boiling by-products resulting in the hydroformylation of propylene in an amount of 18.3% by weight was burned as described in Example 1 using an aqueous 2% sodium hydroxide solution as the absorption liquid 2.

As a result of the combustion, there were recovered 93% of the rhodium and 100% of the phosphorus, as sodium phosphate.

EXAMPLE 3

A toluene solution containing 0.5% by weight of a palladium iodidetriphenylphosphine complex,

$$(PdI_2[P(C_6H_5)_3]),$$

and 19.8% by weight of triphenylphosphine was treated as described in Example 1.

As a result, there were recovered 90% of the palladium and 100% of the phosphorus.

EXAMPLE 4

A toluene solution containing 0.2% by weight of tris(triphenylphosphine)iridium carbonylhydride,

$$(IrH(CO)[P(C_6H_5)_3]_3),$$

and 2.7% by weight of triphenylphosphine was treated as in Example 1.

As a result, there were recovered 91% of the iridium and 100% of the phosphorus.

WHAT WE CLAIM IS:—

1. A process for recovering a noble metal of Group VIII of Mendeléeff's periodic table comprising burning in an oxygen-containing gas an organic solvent solution containing a soluble complex of a Group VIII noble metal which complex contains at least one organophosphorus compound as a ligand, immediately introducing the combustion product into an aqueous absorption liquid to retain therein particles of the Group VIII noble metal and the phosphorus oxide formed by the burning and recovering the noble metal particles from said aqueous liquid.

2. A process as claimed in Claim 1, wherein said aqueous liquid is an alkaline aqueous solution.

3. A process as claimed in Claim 1 or 2, wherein said aqueous liquid contains a carbonaceous adsorption agent suspended therein.

4. A process as claimed in Claim 3, wherein said adsorption agent is activated carbon.

5. A process as claimed in any preceding Claim, wherein the combustion product is directly discharged below the surface of said aqueous liquid.

6. A process as claimed in any preceding Claim, wherein said organic solvent solution is a residue of a reaction mixture obtained in the hydroformylation of an olefin using as a catalyst a soluble complex containing rhodium and a tertiary phosphine and from which the adehyde formed has been removed by distillation.

7. A process as claimed in any preceding Claim, wherein said organic solvent solution is burnt at a temperature of from 1000 to 1500°C.

8. A process as claimed in any preceding Claim, wherein the amount of oxygen contained in said oxygen-containing gas is from 110 to 150% of the theoretical amount required, on a molar basis.

the combustion gas using a blower. A preferred alternative is the submerged combustion method in which the solution as described above is supplied to a burner and burned with oxygen-containing gas such as air, and the resulting combustion product is immediately introduced into the absorption liquid.

An oxygen-containing gas is supplied in an excess amount, such as from 110 to 150 mole %, preferably from 120 to 130 mole %, as oxygen of the theoretical amount required for complete combustion. Air is generally used as the oxygen-containing gas. The combustion temperature is generally adjusted to from 1000 to 1500°C and can also be adajusted by controlling the amount of the oxygen-containing gas supplied, whereby complete combustion can be achieved. Moreover, the volume of the combustion chamber is determined by the amount of liquid to be treated and is generally chosen so as to adjust the residence time of the combustion gas formed in the combustion chamber to from 0.1 to 5.0, preferably from 0.5 to 1.0, seconds.

An arrangement in which the combustion chamber is provided separately from an absorption drum containing the absorption liquid therein and the combustion gas is introduced into the absorption drum through a flue may be employed in the process of this invention. However, an arrangement in which the combustion chamber is provided at the upper portion of the absorption drum and the lower portion of the combustion chamber is submerged in the absorption liquid is usually employed. In the latter case, gas-jet openings are provided at the bottom of the combustion chamber, and are thereby sealed by the absorption liquid. The gas-jet openings are desirably submerged in the liquid to a depth of about 300 to 800 mm below the surface level of the liquid. Where the depth is too great, the increased pressure needed to force air into the combustion chamber requires an economically disadvantageous increase in power; where the depth is too small, the contact time of the formed combustion gas with the absorption liquid is short tending to result in incomplete retention of the phosphorus oxide and noble metal particles in the absorption liquid. Also, when the level of the absorption liquid varies, the pressure in the combustion chamber varies rendering the combustion unstable. Therefore, the level of the absorption liquid is preferably maintained constant by means of an overflow method or by providing a liquid level controller, with removal of surplus liquid.

Any liquid which can absorb the phosphorus oxide gas formed by the combustion may be employed in this invention as the absorption liquid. Generally, water or an alkaline aqueous solution such as sodium carbonate solution, sodium hydroxide solution, potassium carbonate solution, potassium hydroxide solution or calcium hydroxide solution is used. The phosphorus oxide is retained in solution in the liquid as phosphoric acid or a phosphate.

On the other hand, since the Group VIII noble metal is dispersed in the absorption liquid as solid particles, the noble metal can be easily recovered by a conventional method such as filtration or centrifugal separation. Moreover, by dispersing a carbonaceous adsorption agent such as activated carbon, or an organic adsorption agent such as a cellulosic adsorption agent in the absorption liquid, the Group VIII noble metal can be effectively recovered even when the solid particles are very fine.

To facilitate a more complete understanding of the process of the present invention an embodiment thereof will now be described by reference to the accompanying drawing, which is a flow diagram.

In the embodiment a combustion device includes an absorption drum 1 containing absorption liquid 2 and a combustion chamber 3 having a burner 4. The top of the combustion device is connected to a condenser 5 through a conduit 6 and the bottom of the absorption drum 1 is connected to a pump 7 for discharging the absorption liquid 2 through a conduit 8.

Solution containing the organic complex and air are supplied to the burner 4 through conduits 9 and 10, respectively, and burned, by means of the burner 4, in the combustion chamber 3 which is sealed by the absorption liquid 2, and the combustion product formed is immediately introduced into the absorption liquid 2, in which the Group VIII noble metal and phosphorus oxide formed by the combustion are retained. The absorption liquid 2 containing the noble metal and the phosphoric acid or phosphate is withdrawn from the bottom of the absorption drum 1 by means of the pump 7 through the conduit 8 and introduced into a separator 11, wherein the solution is separated into the Group VIII noble metal and the phosphoric acid solution or phosphate solution, which are then passed through a conduit 12 and a conduit 13, respectively. Fresh absorption liquid is supplied to the absorption drum 1 through a conduit 14 in order to maintain the level of the absorption liquid 2 constant. A combustion gas component which is not absorbed in the absorption liquid 2 is introduced through the conduit 6 into the condenser 5, in which the gas component is cooled and is discharged as waste gas after separating mist and condensed water.

As described above in detail, by applying the process of this invention for recovering the Group VIII noble metal from the waste catalyst solution, the Group VIII noble metal is easily recivered in high yield as solid

particles and at the same time the organophosphorus compound is recovered or discharged as innocuous phosphoric acid or phosphate.

The invention will now be illustrated by the following specific Examples.

EXAMPLE 1

Into a drum 1 of a submerged combustion device having an inside capacity of 0.5 m^3 and as shown in the drawing, there was charged 0.3 m^3 of water 2; and to the burner 4 there were supplied through the conduit 9 at a rate of 5 kg/hr a toluene solution containing tris(triphenylphosphine) rhodium carbonylhydride

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A toluene solution containing 0.5% by weight of a palladium iodidetriphenylphosphine complex,

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2. A process as claimed in Claim 1, wherein said aqueous liquid is an alkaline aqueous solution.

3. A process as claimed in Claim 1 or 2, wherein said aqueous liquid contains a carbonaceous adsorption agent suspended therein.

4. A process as claimed in Claim 3, wherein said adsorption agent is activated carbon.

5. A process as claimed in any preceding Claim, wherein the combustion product is directly discharged below the surface of said aqueous liquid.

6. A process as claimed in any preceding Claim, wherein said organic solvent solution is a residue of a reaction mixture obtained in the hydroformylation of an olefin using as a catalyst a soluble complex containing rhodium and a tertiary phosphine and from which the adehyde formed has been removed by distillation.

7. A process as claimed in any preceding Claim, wherein said organic solvent solution is burnt at a temperature of from 1000 to 1500°C.

8. A process as claimed in any preceding Claim, wherein the amount of oxygen contained in said oxygen-containing gas is from 110 to 150% of the theoretical amount required, on a molar basis.

9. A process as claimed in Claim 8, wherein the amount of oxygen is from 120 to 130% on the same basis.

10. A process as claimed in any preceding Claim, wherein the concentration of the noble metal in said organic solvent solution is from 0.05 to 2% by weight, calculated as the noble metal.

11. A process as claimed in any preceding Claim, wherein the concentration of organo phosphorus calculated as phosphorus in said organic solvent solution is from 0.1 to 5% by weight, calculated as phosphorus.

12. A process as claimed in Claim 11, wherein the concentration of organophosphorus calculated as phosphorus in said organic solvent solution is from 0.1 to 2% by weight, calculated as phosphorus.

13. A process as claimed in any preceding Claim, wherein said organic solvent solution contains free organophosphorus compound.

14. A process as claimed in Claim 1 and substantially as herein described.

15. A process for recovering a Group VIII noble metal substantially as herein described with reference to the accompanying drawing or to any one of Examples 1 to 4.

16. A Group VIII noble metal when recovered by a process as claimed in any one of Claims 1 to 15.

17. An aqueous phosphorus-containing solution when recovered by a process as claimed in any one of Claims 1 to 15.

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