

# Hydrocarbonylation in Platinum Metals Metallurgy

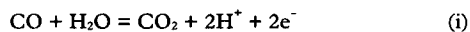
By Professor I. V. Fedoseyev

Kaluga Branch of the Moscow State Technical University, Kaluga, Russia

*For many years we have been studying the reactions of carbon monoxide with chlorocomplexes of the platinum metals in various solutions, such as hydrochloric acid. These hydrocarbonylation reactions result in the formation of various platinum metals carbonyl complexes. Hydrocarbonylation has been used to extract the platinum group metals from the anode muds which remain after the production of copper and nickel. The processes involved, which are described below, produce no waste and therefore do not require special reagents or apparatus. This makes their use very effective for the metallurgy of the platinum group metals. In this paper we discuss the general results of these investigations and some of their applications, such as in the production of powders and catalysts, for which the hydrocarbonylation process is suitable.*

We have been studying the extraction of platinum group metals from the anode mud residues which remain after copper and nickel have been extracted from mineral mined in the nickel-copper sulphide deposits at Noril'sk in the Arctic Circle in North Russia (1).

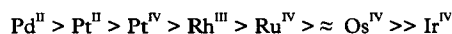
Carbon monoxide is known to react in solution with platinum metal chlorocomplexes. The redox reactions which take place are:



where M is a platinum group metal.

This results in the production of lower valency carbonyl chlorides, carbonyls or metals. The combination of reactions (i) and (ii) is a hydrocarbonylation process of which the kinetics and reaction mechanism are already well known.

The rate of the reaction of carbon monoxide with solutions of chlorocomplexes of the platinum group metals takes place in the following order:



However, there is only limited information available about various technological aspects of the process (2–6). The utilisation of the hydrocarbonylation reaction (for extraction of the plat-

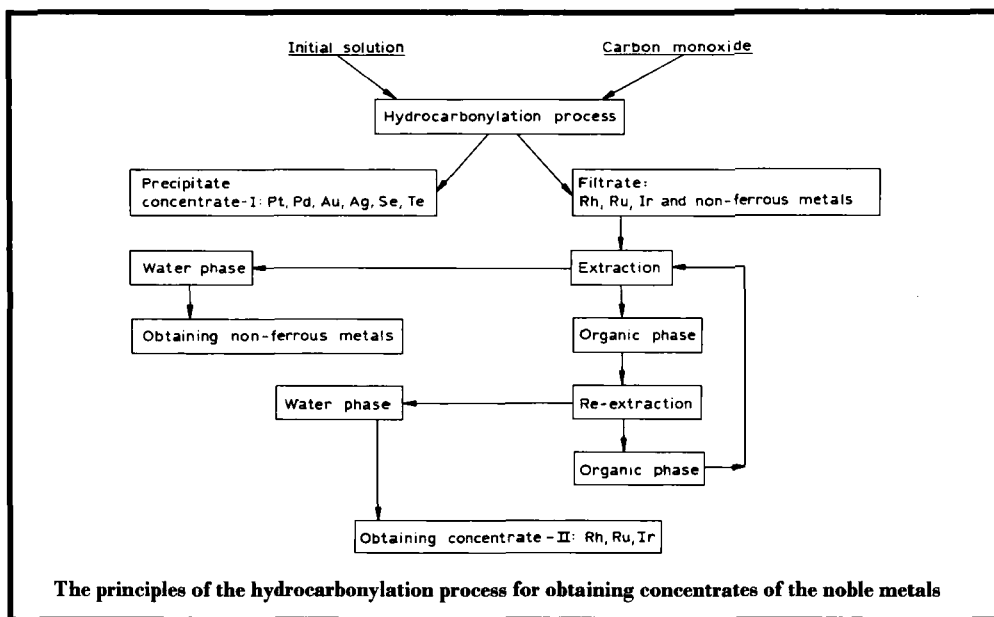
inum group metals) depends on characteristic properties of carbonyl complexes and involves:

- a redox decomposition with formation of the corresponding metal
- extraction of carbonyl complexes in the organic phase
- formation of insoluble substances
- a sorption process

## Selective Concentration of Platinum Group Metals from Anode Muds

The main metals produced in the Noril'sk-Talnakh region within the Arctic Circle in Russia are copper, nickel and the platinum group metals. Noril'sk lies on the northwestern edge of the Siberian platform and is the main source of the platinum group metals in Russia, the other production area being at Pechenga near the Finnish border, and the city of Murmansk in the Kolskiy Peninsula.

After copper and nickel have been extracted the anode muds still contain non-ferrous metals and noble metals. The technology for processing copper-nickel muds has many stages including burning, smelting and electrolysis, and as a result, the platinum metals are distributed among three concentrates, which also contain many non-ferrous metals. One of the



concentrates has, for example, the following composition, in per cent: palladium 35 to 45, platinum 15 to 20, rhodium 0.4 to 0.6, ruthenium 0.08 to 0.15, iridium 0.04 to 0.06, silver 8 to 10, copper 0.7 to 2.5, nickel 0.6 to 2.5, iron 1.5 to 4.0, sulphur 3 to 5, selenium 1 to 1.7 and tellurium 1.5 to 2.5.

Hydrocarbonylation is the principle technology which is then used for obtaining concentrates of the platinum group metals from solutions of anode muds. Such solutions can be

prepared, for example, from the copper and nickel anode muds by the action of chlorine gas, or by addition of hydrochloric acid.

The principles of the hydrocarbonylation process are shown in the Scheme, and the processes were used in our laboratory with copper and nickel anode mud solutions produced by the Noril'sk Nickel Combine, which is the only mining and metallurgical works in that area. The hydrocarbonylation process, used for such complex anode mud solutions, conforms to the

**Table I**  
**Distribution of Noble Metals Produced from the Copper Anode Mud Solution Using the Hydrocarbonylation Process**

Metal	Metal distribution, in per cent, from the initial amount				
	Concentrate-I	Washings	Organic phase	Water phase	Total
Pd	99.97	0.42	0.03	0.04	100.46
Pt	98.32	1.69	0.03	none	100.04
Rh	103.90	none	1.15	none	105.05
Ru	none	7.63	73.00	none	80.63
Ir	none	none	115.20	none	115.20
Au	100.40	none	none	none	100.40
Ag	98.25	none	none	1.15	99.40

**Table II**  
**The Composition of Noble Metals Concentrates Obtained from Copper-Nickel Anode Mud Solutions by the Hydrocarbonylation Process, per cent, per cent**

Experiment number	Pd	Pt	Au	Ag	Rh	Total precious metals	Se	Te	Ni	Fe	Cu	Total non-ferrous metals
1	67.00	14.63	0.02	0.62	0.007	82.48	9.61	5.50	0.200	0.009	0.12	0.15
2	66.17	16.12	none	0.52	0.009	82.84	9.90	5.29	0.004	0.020	0.16	0.18
3	67.35	14.72	none	0.63	0.010	82.73	10.10	5.67	0.019	0.037	0.26	0.32
4	66.20	14.70	none	0.78	0.012	84.71	9.73	5.16	0.012	0.018	0.23	0.26
5	66.75	17.19	none	0.16	0.008	84.13	8.95	5.03	0.009	0.024	0.19	0.22
Average	66.69	15.47	0.02	0.54	0.009	83.37	9.66	5.33	0.013	0.022	0.19	0.22**
Extracted, per cent	>99.9	98.0	100	20.0	0.4*	-	>95	>95	-	-	-	-

\* Ru and Ir are not extracted in the concentrate  
 \*\* the concentrate additionally contains ~ 1% SiO<sub>2</sub>.

usual rules that are obeyed by other binary systems, for example: palladium(II)-copper(II), palladium(II)-iron(III), platinum(II)-copper(II), palladium(II)-platinum(IV) and other similar binary aqueous systems:

(a) before palladium and platinum are precipitated, copper(II) and iron(III) are catalytically reduced to copper(I) and iron(II)

(b) before platinum is precipitated, platinum(IV) is reduced (also catalytically) to platinum(II)

(c) rhodium(III), ruthenium(IV) and iridium(IV) are reduced to the lower carbonylchloride complexes:  $[\text{Rh}(\text{CO})_2\text{Cl}_2]$ ,  $[\text{Ru}(\text{CO})_2\text{Cl}_4]^{2-}$  and  $[\text{Ir}(\text{CO})_2\text{Cl}_2]^-$ , respectively, which are easily extracted by various organic reagents, for example, butyl phosphate.

The metals which are extracted from processing the copper anode mud solution are listed in Table I. Carbon monoxide was added at atmospheric pressure to the initial solution which was held at a temperature of about 100°C for four hours.

The precipitation of rhodium from its various chlorocomplex solutions depends mainly on the temperature and the concentration of the hydrochloric acid. However, the presence of other platinum metals in the solution considerably affects the precipitation of the rhodium. Therefore, we can arrive at a situation where rhodium practically does not precipitate in the first concentrate, concentrate-I, if the hydrocarbonylation

process is carried out at a temperature of 60°C or less, and the concentration of the hydrochloric acid is greater than 1 mol/litre.

Besides platinum, palladium, gold and silver, the metals selenium and tellurium are also precipitated out in concentrate-I. However, Table I shows the composition of concentrate-I after it has been heated to 900°C, which is why the selenium and tellurium are missing.

In order to obtain concentrate-I, from which the metals rhodium, ruthenium and iridium can be extracted, and to study the behaviour of selenium and tellurium during this process, we carried out a series of experiments using the hydrocarbonylation process on a solution of nickel anode muds.

The composition of the nickel anode muds, in grams/litre, was as follows: copper 15.52; nickel 10.47; iron 3.03; sulphate,  $\text{SO}_4^{2-}$ , 16.4; chloride,  $\text{Cl}^-$ , 212.3; and in milligrams/litre the following: selenium 170.6; tellurium 101.8; palladium 1134.0; platinum 321.4; rhodium 41.4; ruthenium 8.67; iridium 3.58; gold 0.17 and silver 86.7. Carbon monoxide was passed through the initial solution, which was held at a temperature below 60°C, and thoroughly mixed for 3 to 4 hours. A black powder (concentrate-I) was obtained. It precipitated easily and was simple to filter. The composition of the obtained concentrates and the proportions of the extracted metals are shown in Table II.

The results of the experiments confirm that by the reaction of carbon monoxide with solutions of copper and nickel anode muds, a high quality platinum-palladium concentrate can be obtained with:

- a high selectivity to the platinum group metals and only small admixture of non-ferrous metals (0.2 to 0.3 per cent)
- a high noble metal concentration (82 to 84 per cent)

Besides the high quality of concentrate-I, it is also possible to achieve a high yield of platinum, palladium, gold, selenium and tellurium in the concentrate.

The process of hydrocarbonylation can be used for selective precipitation of metals from more concentrated solutions. For example, we have

used a solution with the following composition, in grams/litre: platinum 18.4; palladium 51.0; rhodium 6.5; iridium 2.9; gold 1.02; copper 16.2; nickel 3.8; iron 1.90; selenium 2.6; tellurium 3.2 and hydrochloric acid 110. Because of the carbon dioxide, selenium, tellurium, gold and palladium are precipitated; platinum is precipitated at 96 to 98 per cent, but the total amount of rhodium and iridium precipitated is less than 5 per cent. These results therefore confirm the practicality of obtaining platinum group metals concentrates from complex solutions, using the hydrocarbonylation process.

### Regeneration of the Platinum Metals from their Alloys

A considerable quantity of the platinum group metals are in circulation at any one time, and recycling them from their various alloys presents an important technological problem. It has been reported that carbon monoxide can be used to separate rhodium or iridium from the other platinum group metals (3). However, the processes which achieved this were performed in dilute acids, but dissolving the alloys in the hydrochloric acid + chlorine gas system produces solutions containing highly concentrated hydrochloric acid. These must be neutralised by the addition of sodium hydroxide, thus this process produces waste.

We have been investigating the possibility of recovering the platinum metals from solutions containing a high concentration of hydrochloric acid, for systems of the chlorocomplexes of palladium(II)-platinum(IV), platinum(IV)-rhodium(III) and platinum(IV)-iridium(IV). Palladium, platinum and rhodium can be obtained as metallic powders by the action of carbon monoxide on solutions of the single chlorocomplexes in hydrochloric acid. The rate of the reductions is:



This process has an induction period,  $T_{\text{ind}}$ , the duration of which is a function of the type of metal, the temperature and the concentrations of chlorine and hydrogen ions.

Therefore, there is every reason to think that

Table III Results of the Hydrocarbonylation Process in the H <sub>2</sub> PtCl <sub>6</sub> -H <sub>2</sub> RhCl <sub>6</sub> -HCl System						
Composition of the solutions			Experimental conditions		Precipitation of metals, per cent	
Pt <sup>IV</sup> , g/l	Rh <sup>III</sup> , g/l	HCl, M	Temperature, °C	Time, h	Pt	Rh
40.5	30.8	6	75	4	77.5	3.3
29.2	12.3	3	50	4	99.2	2.3
30.2	4.4	4	50	5	99.5	0.9
30.2	4.4	4	25	6	99.7	0.1

Table IV Results of the Hydrocarbonylation Process in the Platinum(IV)-Iridium(IV)-HCl System						
Composition of the solutions			Experimental conditions		Precipitation of metals, per cent	
Pt <sup>IV</sup> , g/l	Ir <sup>IV</sup> , g/l	HCl, M	Temperature, °C	Time, h	Pt	Ir
28.0	23.2	6	75	2.5	99.90	0.08
41.0*	8.5	0.6	75	2.5	99.99	0.24
41.0*	8.5	1.0	75	2.5	99.99	0.10

\* the mixture (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> + (NH<sub>4</sub>)<sub>2</sub>IrCl<sub>6</sub> was used here

Table V Effects of the Hydrocarbonylation Process in the H <sub>2</sub> PtCl <sub>6</sub> -H <sub>2</sub> PdCl <sub>6</sub> -HCl System						
Composition of the solutions			Experimental conditions		Precipitation of metals, per cent	
Pt <sup>IV</sup> , g/l	Pd <sup>II</sup> , g/l	HCl, M	Temperature, °C	Time, h	Pd	Pt
33.2	30.8	6	25	1.0	83.20	3.2
53.2	30.8	6	25	1.5	99.98	6.3
45.0	15.8	6	40	1.5	96.70	2.1
45.0	15.8	8	40	2.0	99.40	3.4
45.0	15.8	6	50	4.0	93.70	2.0
45.0	15.8	6	50	2.0	99.99	3.7
7.2	7.5	4	60	0.5	79.90	7.6
45.0	15.8	6	70	2.5	99.70	8.4
2.0	2.0	3	75	1.0	99.8	10.1

these metals can be separated by modifying the composition of the solution and by adjusting the temperature. Thus, carbon monoxide was bubbled through the initial solutions at atmospheric pressure, while undergoing a thorough

mixing at a temperature of 25 to 75°C.

The composition of the solutions and the experimental data are shown in Tables III to V. Our assumption was confirmed for the systems platinum(IV)-rhodium(III) and platinum(IV)-

**Table VI**  
**The Effects of the Preparation Conditions on the Characteristics of the Palladium Powders**

Sample	Experimental conditions			Specific surface, m <sup>2</sup> /g	Volume density, g/cm <sup>3</sup>
	Pd(II), g/l	HCl, M	Temperature, °C		
1	44.0	2	35	9.1	0.91
2	50.0	1	80	4.2	1.34
3	55.0	1	80	3.1	1.89
4	76.0	1	80	1.7	2.11
5	46.0	6	80	0.74	2.60

iridium(IV): in both cases platinum can be almost completely precipitated with only a little admixture of the other platinum metal.

However, a different reaction occurred in the platinum(IV)-palladium(II) system where up to about 10 weight per cent of platinum, together with palladium, is precipitated over a wide range of temperatures and hydrochloric acid concentrations, see Table V. This is probably due to the formation of rather stable heteronuclear carbonyl complexes of palladium-platinum.

### Preparation of Palladium and Platinum Powders

Metallic powders of palladium, platinum and their alloys find wide application in the electronics industry. They are obtained by the reduction of corresponding solutions using, for example, hydrazine.

We have studied the possibility of utilising the hydrocarbonylation process for obtaining platinum metals powders with the required physicochemical properties for these uses, such as specific surface area, volume density, dispersion and resistance to oxidation.

For palladium, the rate of reduction in the Pd(II)-H<sup>+</sup>-Cl<sup>-</sup>-H<sub>2</sub>O-CO system can be expressed in the following way (7):

$$dC_{Pd}/d\tau = K \cdot C_{Pd}^{II} \cdot C_{H^+}^{-2} \cdot C_{Cl^-}^{-1} \cdot C_{H_2O}^2 \cdot C_{CO}$$

where C represents the concentration of each component in the system and K is the reaction constant for this particular reduction,  $\tau$  is time.

By using the concentrations of palladium and hydrochloric acid, and the temperature as the variables, we have obtained the equation of the regression, which correlates these parameters with the value of the volume density of the palladium powders. Experimental results are shown in Table VI.

Analysis of the experimental data has enabled us to produce palladium powders with the necessary physicochemical properties for use in electronics, according to the following rules:

- for powders with low volume density and small particle size, the hydrocarbonylation process should be performed at room temperature in low concentrations of hydrochloric acid;
- to obtain powders with greater volume density and larger particle size, the hydrocarbonylation should be carried out at about 80°C in high concentrations of hydrochloric acid.

For electronic applications palladium powders must be thermally stable. To test for this, samples of palladium powders were investigated by thermography. The samples were distributed into two groups:

- (i) thermally stable powders having oxidation temperatures higher than 500°C with the proportion of oxidised palladium being around 20 to 30 per cent
- (ii) thermally unstable powders having oxidation temperatures of 200 to 280°C with the proportion of oxidised palladium being above 70 per cent.

From all the experimental data, we have

**Table VII**  
**Thermomechanical Data of Platinum Wire**  
**1 mm in Diameter Containing + 0.25 weight per cent Zirconia**

Sample	$\sigma_b$ , MPa		$\sigma$ , per cent		Temperature, 1100°C			
	20°C	1100°C	20°C	1100°C	Loading, MPa	Time to gap, min	$\epsilon$ , per cent	$\sigma_{0.2}$
1*	350	60	8	8	50 → 45	7	17	58.5
2**	293	60	14	4	40	32	7.5	56

\*The wire was first annealed in hydrogen at 950°C for 30 minutes

\*\* The wire was first annealed in vacuum at 1100°C for 20 minutes

$\sigma_b$  strength (limit)

$\sigma$  the stretch of the sample at the moment of destruction (in per cent)

$\epsilon$  relative strain

$\sigma_{0.2}$  conventional tensile yield limit

"Time to gap" is the time needed for the destruction of the sample

concluded that palladium powders, suitable for use in electronic applications, can be produced by the hydrocarbonylation process.

#### Alloy Powders

Using the hydrocarbonylation process for the production of platinum and palladium alloy powders has also been examined. A solution of  $H_2PtCl_4$  and  $H_2PdCl_4$  was reacted with carbon monoxide under atmospheric pressure at a temperature of around 80°C for three to five hours. Phase analysis showed that the alloy powders obtained were solid solutions with a concentration of chlorine ions less than 0.005 weight per cent (8).

#### Dispersion Strengthened Material

The hydrocarbonylation process may also be used for obtaining dispersion strengthened materials, such as platinum-zirconium oxide. A pow-

der of platinum and 0.25 weight per cent zirconium oxide was obtained by hydrocarbonylation from initial solutions containing platinum(IV) and zirconium oxide. From this powder, a resulting compact metal was produced, having a hardness of 137.2 to 142.6 HV. The results of thermomechanical tests are given in Table VII.

#### Preparation of Supported Catalysts

Redox decomposition of the carbonylchloride complexes of palladium(I), platinum(I) and rhodium(I) was used for the preparation of supported catalysts. A catalyst containing 3 weight per cent palladium supported on alumina was prepared by the decomposition of water-organic solutions of the palladium(I) carbonylchloride complex on alumina. This palladium/alumina material was then tested as a hydrogenation

**Table VIII**  
**Test Results of Palladium and Platinum Catalysts for the Reduction of Propylene into Glycols**

Sample	Support	Catalyst composition*, mol	Relative activity	Selectivity, per cent
1	TiO <sub>2</sub>	Pd : Pt = 7.8 : 1	96	75
2		Pd : Pt = 6.5 : 1	116	80
3		Pd : Pt = 6.0 : 1	128	85
4	charcoal	Pd : Pt = 6.0 : 1	66	78
5		Pd : Pt = 7.5 : 1	74	76

\* All samples contained 3 weight per cent of the metals

Relative activity is the catalyst activity with regard to some standard sample

catalyst for phenylacetylene. It had high activity and produced more than 10 litres of  $H_2$ /min/g Pd with 94.5 per cent selectivity (9). This is better than results from the same catalyst which has been produced by other methods.

Catalysts with supports such as titania and charcoal, were obtained using the same method from binary solutions of the carbonylchloride complexes of the platinum metals (platinum and palladium). Results of tests using them are shown in Table VIII. These catalysts have the same activity and selectivity as catalysts prepared by standard methods, however, their method of production is simpler.

### Conclusions

Thus, the results of our investigations show that the hydrocarbonylation process and carbonyl complexes of the platinum metals can

be used for the concentration, extraction and refining of the platinum group metals. The use of these processes for the production of composite materials and processing by powder metallurgical methods offers a potentially successful alternative to current means of production. However, as yet, these methods have not been put to industrial use.

### References

- 1 *Platinum Metals Rev.*, 1991, 35, (2), 96
- 2 *French Patent* 2,305,398; 1976
- 3 *British Patent* 1,472,176; 1977
- 4 *British Patent* 1,507,792; 1978
- 5 *U.S. Patent* 4,163,664; 1979
- 6 *Russian Patent* 1,637,352; 1990
- 7 V. I. Spitzyn, I. V. Fedoseyev and I. V. Znamensky, *J. Inorg. Chem.*, 1980, 25, (10), 2754
- 8 *Russian Patent* 1,541,894; 1989
- 9 *Russian Patent* 1,593,008; 1990

## Single Platinum-Rhodium Gauze for Partial Oxidation

The possibility of using a small reactor for converting the light alkanes found in remote natural gases into more useful liquid fuels and commercial products, by an efficient and fast process, has been suggested in work performed by scientists at the University of Minnesota (D. A. Goetsch and L. D. Schmidt, "Microsecond Catalytic Partial Oxidation of Alkanes", *Science*, 1996, 271, (5255), 1560–1562).

Using a single layer of woven platinum-10 per cent rhodium gauze, they were able to perform catalytic reactions of microsecond duration at atmospheric pressures with very high reaction rates. This allowed selective partial oxidation of the reactants to take place. Reacting gases were heated from room temperature to  $> 800^\circ\text{C}$ , on entering the single layer of gauze, for a contact time of 8 to 500  $\mu\text{s}$ . After reaction the products were rapidly quenched from  $800^\circ\text{C}$  to  $\sim 400^\circ\text{C}$  within 200  $\mu\text{s}$ , as they mixed with the cold unreacted gases that had passed between the gauze wires of the catalyst. This allows selective production and survival of oxygenates.

A single Pt gauze catalyst layer produces high oxygen conversions and very different selectivities from coated monoliths or multiple gauzes, with parent olefin, formaldehyde and acetaldehyde being the most partially oxidated products. For ethane, propane, *n*-butane and isobutane different reactivities and selectivities were observed: selectivity to olefins strongly decreased, while selectivity to oxygenates increased with

alkyl chain length. At least 40% of reacted butane was converted, mostly to formaldehyde and acetaldehyde.

Steady conversions and selectivities were reached after several hours, with temperatures at  $> 800^\circ\text{C}$ . The near-adiabatic conditions prevent carbon formation.

Besides being used as a single gauze, the gauze may also be used to preheat gases for partial oxidation by oxide catalysts, such as  $V_2O_5$ . These catalysts produce partially oxidised products with high selectivity and require very high ignition temperatures, so preheating is necessary for high conversions and adiabatic operation. A single platinum gauze, placed in front of the oxide catalyst, could preheat the gases to the required temperature. Rapid quenching would keep the conversion low so alkanes and oxygen would remain for reaction on the catalyst.

The reactor has also been operated at 70 m/s, which suggests that sonic flow could be obtained, with supersonic quenching. This increased speed of reaction might further stabilise useful chemical species.

At present, the reactors are producing  $\sim 20$  kg/day of aldehydes and butylene from butane. A reactor of 0.3 m diameter could produce  $\sim 1000$  metric tons/day at 70 m/s under these conditions. With higher pressures and velocities, and if products are removed and reactants added between catalyst layers, even higher yields and greater selectivities may result.