The Cativa™ Process for the Manufacture of Acetic Acid

IRIDIUM CATALYST IMPROVES PRODUCTIVITY IN AN ESTABLISHED INDUSTRIAL PROCESS

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Acetic acid is an important industrial commodity chemical, with a world demand of about 6 million tonnes per year and many industrial uses. The preferred industrial method for its manufacture is by the carbonylation of methanol and this accounts for approximately 60 per cent of the total world acetic acid manufacturing capacity. The carbonylation of methanol, catalysed by rhodium, was invented by Monsanto in the 1960s and for 25 years was the leading technology. In 1996 a new, more efficient, process for the carbonylation of methanol was announced by BP Chemicals, this time using an iridium catalyst. This article describes the new process and looks at the ways in which it improves upon the prior technology.

In 1996 a new process for the carbonylation of methanol to acetic acid was announced by BP Chemicals, based on a promoted iridium catalyst package, named Cativa™. The new process offers both significant improvements over the conventional rhodium-based Monsanto technology and significant savings on the capital required to build new plants or to expand existing methanol carbonylation units. Small-scale batch testing of the new Cativa™ process began in 1990, and in November 1995 the process was first used commercially, in Texas City, U.S.A., see Table I.

The new technology was able to increase plant throughput significantly by removing previous process restrictions (debottlenecking), for instance at Hull, see Figure 1. The final throughput achieved has so far been determined by local availability of carbon monoxide, CO, feedstock rather than any limitation imposed by the Cativa™ system. In 2000 the first plant to use this new technology will be brought on-stream in Malaysia. The rapid deployment of this new iridium-based technology is due to these successes and its many advantages over rhodium-based technology. The background to this industrial method of producing acetic acid is explained below.

The Rhodium-Based Monsanto Process

The production of acetic acid by the Monsanto process utilises a rhodium catalyst and operates at a pressure of 30 to 60 atmospheres and at temperatures of 150 to 200°C. The process gives selectivity of over 99 per cent for the major feed-


Table I

Plants Producing Acetic Acid Using the New Cativa™ Promoted Iridium Catalyst Package

Plant	Location	Year	Debottlenecking or increased throughput achieved, %
Sterling Chemicals	Texas City, U.S.A.	1995	20
Samsung-BP	Ulsan, South Korea	1997	75
BP Chemicals	Hull, U.K.	1998	25
Sterling Chemicals	Texas City, U.S.A.	1999	25
BP Petronas	Kertih, Malaysia	2000	Output 500,000 tonnes per annum

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stock, methanol (1). This reaction has been investigated in great detail by Forster and his co-workers at Monsanto and the accepted mechanism is shown in Scheme I (2). The cycle is a classic example of a homogeneous catalytic process and is made up of six discrete but interlinked reactions.

During the methanol carbonylation, methyl iodide is generated by the reaction of added methanol with hydrogen iodide. Infrared spectroscopic studies have shown that the major rhodium catalyst species present is $[Rh(CO)_2I_2]^-$, A. The methyl iodide adds oxidatively to this rhodium species to give a rhodium-methyl complex, B. The key to the process is that this rhodium-methyl complex undergoes a rapid change in which the methyl is shifted to a neighbouring carbonyl group, C. After the subsequent addition of CO, the rhodium complex becomes locked into this acyl form, D. Reductive elimination of the acyl species and attack by water can then occur to liberate the original rhodium dicarbonyl diiodide complex

Fig. 1 The Cativa™ acetic acid plant which is now operating at Hull. The plant uses a promoted iridium catalyst package for the carbonylation of methanol. The new combined light ends and drying column can be seen

Scheme I

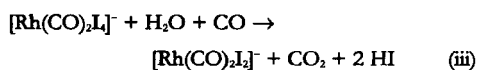*The reaction cycle for the Monsanto rhodium-catalysed carbonylation of methanol to acetic acid*
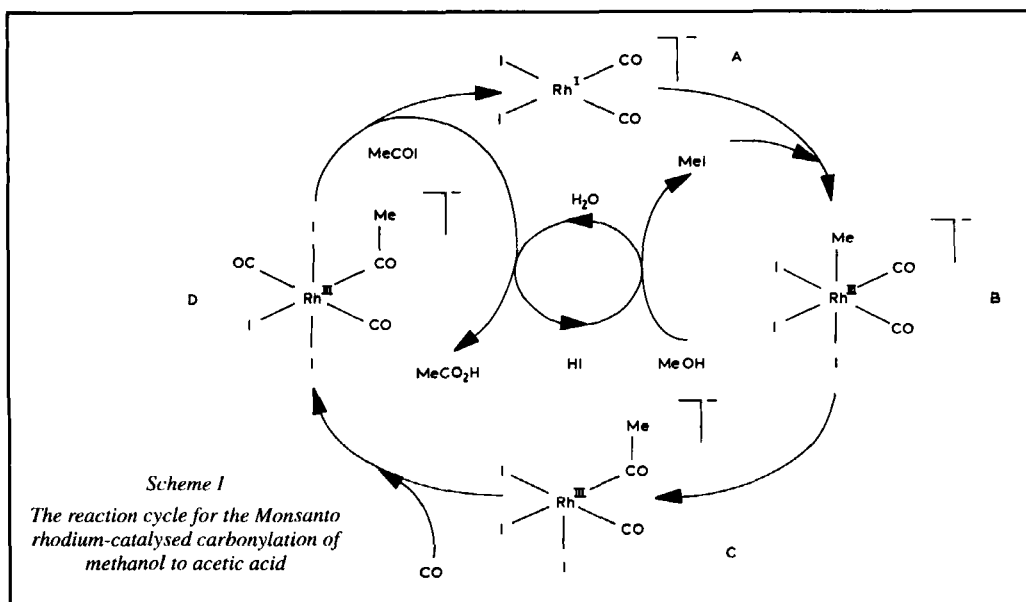
and to form acetic acid and hydrogen iodide, HI.

When the water content is high (> 8 wt.%), the rate determining step in the process is the oxidative addition of methyl iodide to the rhodium centre. The reaction rate is then essentially first order in both catalyst and methyl iodide concentrations, and under commercial reaction conditions it is largely independent of any other parameters:

$$\text{Rate} \propto [\text{catalyst}] \times [CH_3I] \qquad \text{(i)}$$

However, if the water content is less than 8 wt.%, the rate determining step becomes the reductive elimination of the acyl species, from catalyst species D.

Although rhodium-catalysed carbonylation of methanol is highly selective and efficient, it suffers from some disadvantageous side reactions. For example, rhodium will also catalyse the water gas shift reaction. This reaction occurs via the competing oxidative addition of HI to $[Rh(CO)_2I_2]^-$ and generates low levels of carbon dioxide, CO_2, and hydrogen, H_2, from CO and water feed.

$$[Rh(CO)_2I_2]^- + 2HI \rightarrow [Rh(CO)_2I_4]^- + H_2 \qquad \text{(ii)}$$

$$[Rh(CO)_2I_4]^- + H_2O + CO \rightarrow$$
$$[Rh(CO)_2I_2]^- + CO_2 + 2 HI \qquad \text{(iii)}$$

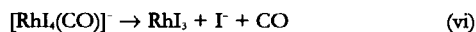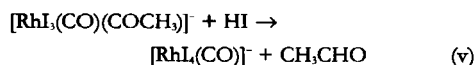$$\text{Overall:} \quad CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(iv)}$$

This side reaction represents a loss of selectivity with respect to the CO raw material. Also, the gaseous byproducts dilute the CO present in the reactor, lowering its partial pressure – which would eventually starve the system of CO. Significant volumes of gas are thus vented – with further loss of yield as the reaction is dependent upon a minimum CO partial pressure. However, the yield on CO is good (> 85 per cent), but there is room for improvement (3, 4).

Propionic acid is the major liquid byproduct from this process and may be produced by the carbonylation of ethanol, present as an impurity in the methanol feed. However, much more propionic acid is observed than is accounted for by this route. As this rhodium catalysed system can generate acetaldehyde, it is proposed that this acetaldehyde, or its rhodium-bound precursor, undergoes reduction by hydrogen present in the

system to give ethanol which subsequently yields propionic acid.

One possible precursor for the generation of acetaldehyde is the rhodium-acyl species, D, shown in Scheme I. Reaction of this species with hydrogen iodide would yield acetaldehyde and $[RhI_4CO]^-$, the latter being well known in this system and proposed to be the principal cause of catalyst loss by precipitation of inactive rhodium triiodide. The precipitation is observed in CO-deficient areas of the plant.

$$[RhI_3(CO)(COCH_3)]^- + HI \rightarrow$$
$$[RhI_4(CO)]^- + CH_3CHO \qquad \text{(v)}$$

$$[RhI_4(CO)]^- \rightarrow RhI_3 + I^- + CO \qquad \text{(vi)}$$

In addition to propionic acid, very small amounts of acetaldehyde condensation products, their derivatives and iodide derivatives are also observed. However, under the commercial operating conditions of the original Monsanto process, these trace compounds do not present a problem to either product yield or product purity. The major units comprising a commercial-scale Monsanto methanol carbonylation plant are shown in Figure 2.

The Monsanto Industrial Configuration

The carbonylation reaction is carried out in a stirred tank reactor on a continuous basis. Liquid is removed from the reactor through a pressure reduction valve. This then enters an adiabatic flash tank, where the light components of methyl acetate, methyl iodide, some water and the product acetic acid are removed as a vapour from the top of the vessel. These are fed forward to the distillation train for further purification. The remaining liquid in the flash tank, which contains the dissolved catalyst, is recycled to the reactor. A major limitation of the standard rhodium-catalysed methanol carbonylation technology is the instability of the catalyst in the CO-deficient areas of the plant, especially in the flash tank. Here, loss of CO from the rhodium complexes formed can lead to the formation of inactive species, such as $[Rh(CO)_2I_2]^-$, and eventually loss of rhodium as the insoluble RhI_3, see Equations (v) and (vi).

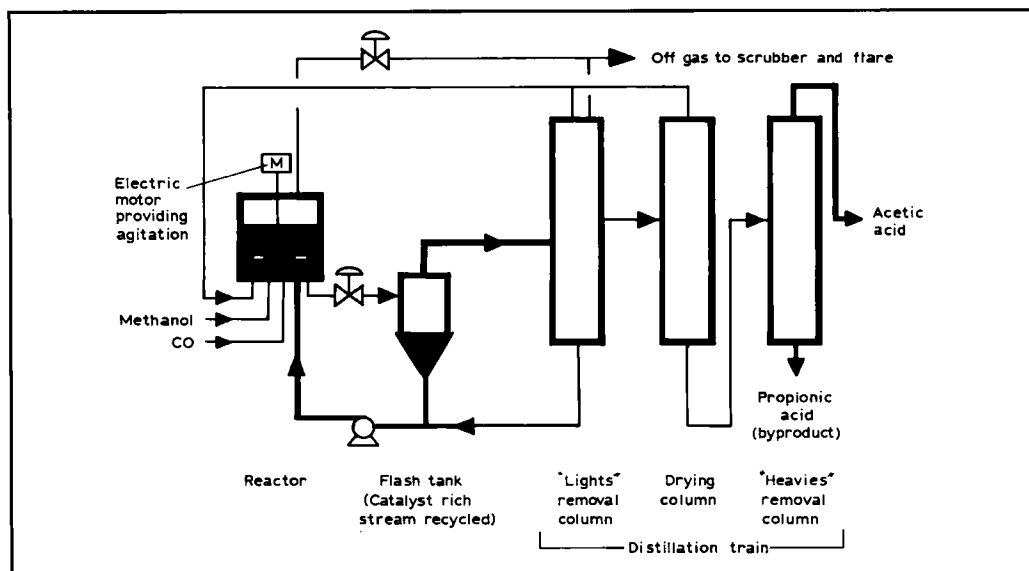Conditions in the reactor have to be maintained

Fig. 2 *The major units comprising a commercial-scale Monsanto methanol operating plant, which uses a rhodium-based catalyst. The technology uses three distillation columns to sequentially remove low boilers (methyl iodide and methyl acetate), water, and high boilers (propionic acid) and deliver high purity acetic acid product*

within certain limits to prevent precipitation of the catalyst. This imposes limits on the water, methyl acetate, methyl iodide and rhodium concentrations. A minimum CO partial pressure is also required. To prevent catalyst precipitation and achieve high reaction rates, high water concentrations in excess of 10 wt.% are desirable. These restrictions place a limit on plant productivity and increase operating costs since the distillation section of the plant has to remove all the water from the acetic acid product for recycling to the reactor. (The water is recycled to maintain the correct standing concentration.)

Significant capital and operational costs are also incurred by the necessity of operating a large distillation column (the "Heavies" column) to remove low levels of high boiling point impurities, with propionic acid being the major component.

The Cativa™ Iridium Catalyst for Methanol Carbonylation

Due to the limitations described above and also because of the very attractive price difference between rhodium ($5200 per troy oz) and iridium ($300 per troy oz) which existed in 1990, research into the use of iridium as a catalyst was resumed by

BP in 1990, after earlier work by Monsanto. The initial batch autoclave experiments showed significant promise, and the development rapidly required the coordinated effort of several diverse teams.

One early finding from the investigations was of the extreme robustness of the iridium catalyst species (5). Its robustness at extremely low water concentrations (0.5 wt.%) is particularly significant and ideal for optimisation of the methanol carbonylation process. The iridium catalyst was also found to remain stable under a wide range of conditions that would cause the rhodium analogues to decompose completely to inactive and largely irrecoverable rhodium salts. Besides this stability, iridium is also much more soluble than rhodium in the reaction medium and thus higher catalyst concentrations can be obtained, making much higher reaction rates achievable.

The unique differences between the rhodium and iridium catalytic cycles for methanol carbonylation have been investigated in a close partnership between researchers from BP Chemicals in Hull and a research group at the University of Sheffield (6). The anionic iridium cycle, shown in Scheme II, is similar to the rhodium cycle, but contains

Scheme II

Catalytic cycle for the carbonylation of methanol using iridium
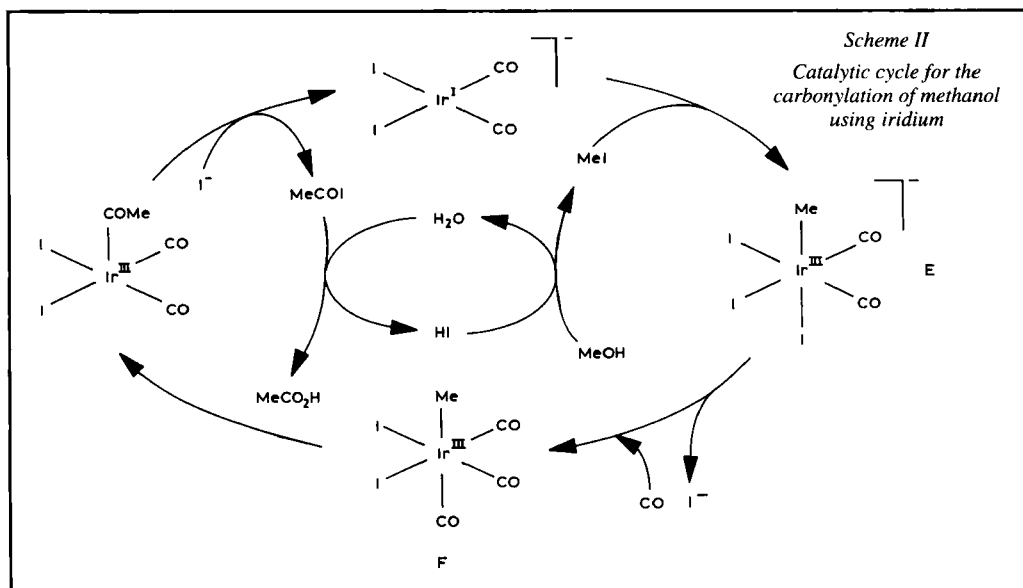
sufficient key differences to produce the major advantages seen with the iridium process.

Model studies have shown that the oxidative addition of methyl iodide to the iridium centre is about 150 times faster than the equivalent reaction with rhodium (6). This represents a dramatic improvement in the available reaction rates, as this step is now no longer rate determining (as in the case of rhodium). The slowest step in the cycle is the subsequent migratory insertion of CO to form the iridium-acyl species, F, which involves the elimination of ionic iodide and the coordination of an additional CO ligand. This would suggest a totally different form of rate law:

$$\text{Rate} \propto \frac{[\text{catalyst}] \times [\text{CO}]}{[\text{I}^-]} \qquad \text{(vii)}$$

or, taking the organic equilibria into account:

$$\text{Rate} \propto [\text{catalyst}] \times [\text{CO}] \times [\text{MeOAc}] \qquad \text{(viii)}$$

The implied inverse dependence on ionic iodide concentration suggests that very high reaction rates should be achievable by operating at low iodide concentrations. It also suggests that the inclusion of species capable of assisting in removing iodide should promote this new rate limiting step. Promoters for this system fall within two distinct groups:

- simple iodide complexes of zinc, cadmium, mercury, gallium and indium (7), and
- carbonyl-iodide complexes of tungsten, rhenium, ruthenium and osmium (8, 9).

Batch Autoclave Studies

The effect on the reaction rate of adding five molar equivalents of promoter to one of the iridium catalyst is shown in Table II. A combination of promoters may also be used, see runs 13 and 14. None of these metals are effective as carbonylation catalysts in their own right, but all are effective when used in conjunction with iridium.

The presence of a promoter leads to a substantial increase in the proportion of "active anionic" species $[\text{Ir(CO)}_2\text{I}_3\text{Me}]^-$, E, and a substantial decrease in the "inactive" $[\text{Ir(CO)}_2\text{I}_4]^-$. A suggested mechanism for the promotion of iridium catalysis by a metal promoter $[\text{M(CO)}_x\text{I}_y]$, is given in Scheme III. The promotion is thought to occur via direct interaction of promoter and iridium species as shown. The rate of reaction is dependent upon the loss of iodide from $[\text{Ir(CO)}_2\text{I}_3\text{Me}]^-$. These metal promoters are believed to reduce the standing concentration of I^- thus facilitating the loss of iodide from the catalytic species. It is also postulated that carbonyl-based promoters may then go on to donate CO in further steps of the catalytic cycle.

Effect of Various Additives on the Rate for the Iridium-Catalysed Carbonylation of Methanol[a] from Batch Autoclave Data

Experimental run	Additive	Additive:iridium, molar ratio	Carbonylation rate, mol dm^{-3} h^{-1}
1	None	–	8.2
2	LiI	1:1	4.3
3	Bu$_4$NI	1:1	2.7
4	Ru(CO)$_4$I$_2$	5:1	21.6
5	Os(CO)$_4$I$_2$	5:1	18.6
6	Re(CO)$_5$Cl	5:1	9.7
7	W(CO)$_6$	5:1	9.0
8	ZnI$_2$	5:1	11.5
9	CdI$_2$	5:1	14.7
10	HgI$_2$	5:1	11.8
11	GaI$_3$	5:1	12.7
12	InI$_3$	5:1	14.8
13	InI$_3$/Ru(CO)$_4$I$_2$	5:1:1	19.4
14	ZnI$_2$/Ru(CO)$_4$I$_2$	5:1:1	13.1
15	Ru(CO)$_4$I$_2$	Control: no iridium[b]	0[c]

[a] *Reaction conditions: 190°C, 22 barg, and 1500 rpm. Autoclave charge: methyl acetate (648 mmol), water (943 mmol), acetic acid (1258 mmol), methyl iodide (62 mmol), and H$_2$IrCl$_6$ (1.56 mmol) plus additive as required. Carbonylation rate, in mol dm^{-3} h^{-1}, measured at 50 per cent conversion of methyl acetate.*

[b] *Control experiment conducted in the absence of iridium. Amount of the ruthenium complex used is the same as in run 4.*

[c] *No CO uptake observed*

Another key role of the promoter appears to be in the prevention of the build up of "inactive" forms of the catalyst, such as [Ir(CO)$_2$I$_4$]$^-$ and [Ir(CO)$_3$I$_3$]. These species are formed as intermediates in the water gas shift reaction.

For the rhodium system the rate of the carbonylation reaction is dependent only upon the concentrations of rhodium and methyl iodide. However, the situation is more complex for the promoted iridium system. Table III illustrates the effect of the system parameters on the rate of reaction.

The effect of water concentration on the carbonylation rates of a rhodium system and an iridium/ruthenium system is illustrated in Figure 3. For rhodium, a decline in carbonylation rate is observed as the water content is reduced below about 8 wt.%. There are a number of possible theories for this, including a possible build up of the "inactive" [Rh(CO)$_2$I$_4$]$^-$ species formed in the water gas shift cycle at lower water concentrations,
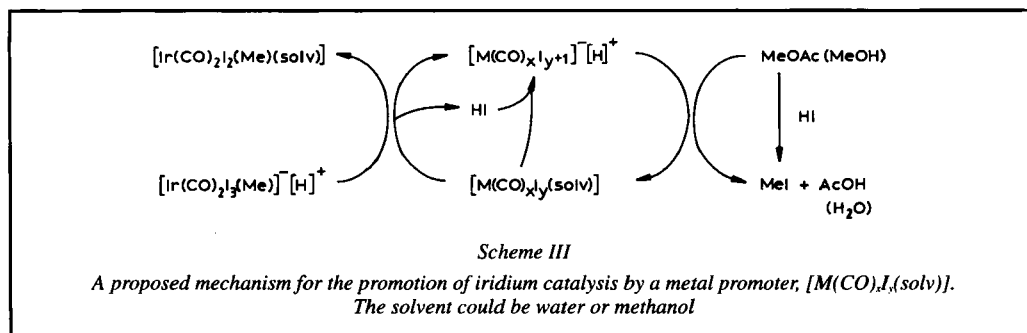

Scheme III

A proposed mechanism for the promotion of iridium catalysis by a metal promoter, [M(CO)$_x$I$_y$(solv)]. The solvent could be water or methanol

Table III

The Rate Dependence Differences between the Rhodium and Iridium Systems

	Rhodium	Iridium/promoter
Water	1st order below 8 wt.% Independent above 8 wt.%	Increases with increasing water up to ~ 5 wt.%, then decreases with increasing water
Methyl acetate	Independent above ~ 1 wt.%	Increases with increasing methyl acetate
Methyl iodide	1st order	Increases with increasing methyl iodide up to ~ 6 wt.%, then independent
CO partial pressure	A minimum CO partial pressure is required; above this, independent	Increases with increasing CO partial pressure. As the CO partial pressure falls below ~ 8 bara the rate decreases more rapidly
Corrosion metals	Independent	As the corrosion metals increase in concentration, the rate decreases
Rhodium	1st order	Non applicable
Iridium	Non applicable	1st order, effect tails off at high catalyst concentrations
Promoter	Non applicable	Increases with increasing promoter, effect tails off at higher concentrations

bara is bar absolute; atmospheric pressure = 1 bar absolute (= 0 bar gauge, barg)

which is a precursor for the formation of insoluble RhI_3.

Another theory for the decline in the carbonylation rate is that the rate determining step in the catalytic cycle changes to the reductive elimination (attack by water) instead of oxidative addition. This is consistent with the increased amount of acetaldehyde-derived byproducts in a low water concentration rhodium system, as the rhodium-acyl species, **D**, is longer lived.

At lower water concentrations, the addition of ionic iodides, especially Group I metal iodides, to the process has been found to stabilise the rhodium catalysts and sustain the reaction rate by inhibiting the water gas shift cycle, inhibiting the formation of $[Rh(CO)_2I_4]^-$ and its degradation to RhI_3 and promoting the oxidative addition step of the catalytic cycle (10–13).
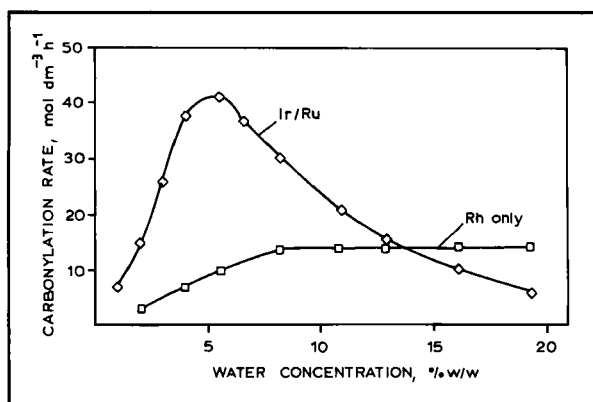

Fig. 3 A comparison of carbonylation rates for iridium/ruthenium and rhodium processes depending on water concentration. These batch autoclave data were taken under conditions of ~ 30 % w/w methyl acetate, 8.4 % w/w methyl iodide, 28 barg total pressure and 190°C; (barg is a bar gauge, referenced to atmospheric pressure, with atmospheric pressure = 0 bar gauge)

Fig. 4 The effect of catalyst concentration on the carbonylation rate for an unpromoted and a ruthenium-promoted iridium catalyst. The ruthenium promoter is effective over a wide range of catalyst concentrations. Batch autoclave data were taken at ~ 20 % w/w methyl acetate, 8 % w/w methyl iodide, 5.7 % w/w water, 28 barg total pressure and 190°C
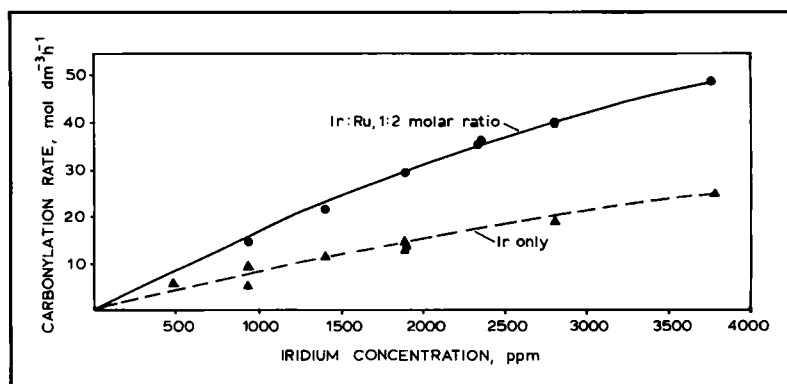
However, there is also a downside, in the lithium-promoted rhodium system, the acetaldehyde is not scavenged sufficiently by the catalyst system to form propionic acid and therefore the concentration of acetaldehyde increases, condensation reactions occur and higher non-acidic compounds and iodide derivatives are formed, for example hexyl iodide. Further purification steps are then required (14).

For a Cativa™ system, in contrast to rhodium, the reaction rate increases with decreasing water content, see Figure 3. A maximum value is reached at around 5 % w/w (under the conditions shown). Throughout this region of the curve the iridium species observed are [Ir(CO)₂I₄]⁻ (the "inactive" species which is formed in the water gas shift cycle) and [Ir(CO)₂I₃Me]⁻ (the "active" species in the anionic cycle). When the water concentration falls below 5 % w/w the carbonylation rate declines and the neutral "active" species [Ir(CO)₃I] and the corresponding "inactive" water gas shift species [Ir(CO)₃I₃] are observed.

Other Factors Affecting the Reaction Rate
(i) Methyl acetate concentration

In the rhodium system, the rate is independent of the methyl acetate concentration across a range of reactor compositions and process conditions (1). In contrast, the Cativa™ system displays a strong rate dependence on methyl acetate concentration, and methyl acetate concentrations can be increased to far higher levels than in the rhodium system, leading to high reaction rates. High methyl acetate concentrations may not be used in the rhodium process because of catalyst precipitation in downstream areas of the plant.

(ii) Methyl iodide concentration

The reaction rate for Cativa™ has a reduced dependency on the methyl iodide concentration compared with the rhodium system. This is consistent with the fast rate of oxidative addition of methyl iodide to [Ir(CO)₂I₂]⁻ giving [Ir(CO)₂I₃Me]⁻.

(iii) CO partial pressure

The effect of CO partial pressure in the Cativa™ process is more significant than for the rhodium process with the rate being suppressed below 8 bara when operating in the ionic cycle.

(iii) Poisoning the Cativa™ system

Corrosion metals, primarily iron and nickel, poison the Cativa™ process. However, it is not the corrosion metals themselves that poison the process, but rather the ionic iodide which they support that inhibits the iodide loss step in the carbonylation cycle, see Scheme II.

(iv) Catalyst concentration

The effects of catalyst concentrations on the carbonylation rate for an unpromoted and for a ruthenium-promoted iridium catalyst are shown in Figure 4. The ruthenium promoter is effective over a wide range of catalyst concentrations. As high catalyst concentrations and high reaction rates are approached a deviation from first order behaviour is noted, and a small but significant loss in reaction selectivity is observed.

(v) Promoters

The addition of further promoters, to the ones already present, for example iridium/ruthenium, can have positive effects. For instance, a synergy is

Table IV

Effect of Lithium Iodide Additions on the Carbonylation Rate for Iridium and Iridium/Ruthenium Catalysed Methanol Carbonylation[a] from Batch Autoclave Data

Experimental run	Catalyst system	Water, % w/w	Carbonylation rate, mol dm^{-3} h^{-1}
1	Iridium only	2.1	12.1
2	Iridium/lithium 1:1 molar ratio	2.0	6.3
3	Iridium/ruthenium 1:2 molar ratio	2.0	15.1
4	Iridium/ruthenium/lithium 1:2:1 molar ratio	2.0	30.8

[a] *Reaction conditions: 190°C, 28 barg total pressure, and 30 % w/w methyl acetate, 8.4 % w/w methyl iodide and 1950 ppm iridium*

observed between the promoters and iodide salts, such as lithium iodide (15). Iodides usually poison the iridium catalyst, for example, if lithium iodide is added to an iridium-only catalyst at low water (~ 2 % w/w) and high methyl acetate (30 % w/w), there is a markedly reduced carbonylation rate. A ratio of one molar equivalent of lithium iodide: iridium reduces the reaction rate by 50 per cent, see run 2 in Table IV but, under the same reaction conditions two molar equivalents of ruthenium: iridium increases the carbonylation rate by 25 per cent. Remarkably, adding lithium iodide to the ruthenium-promoted catalyst under these conditions further doubles the carbonylation rate (run 4). The net effect is that ruthenium and lithium iodide in combination under certain conditions increase the reaction rate by 250 per cent with respect to an unpromoted iridium catalyst. Thus, adding low levels of iodide salts to a promoted iridium catalyst allows the position of the rate maximum, with respect to the water concentration,

to be moved to even lower water.

The effect of the lithium iodide:iridium molar ratio on the carbonylation rate is shown in Figure 5 for a ruthenium-promoted iridium catalyst, having iridium:ruthenium molar ratios of 1:2 and 1:5. Under these conditions an exceptionally high rate of 47 mol dm^{-3} h^{-1} can be achieved with a molar ratio for iridium:ruthenium:lithium of 1:5:1.

Interdependence of Process Variables

The Cativa™ process thus displays a complex interdependence between all the major process variables, notably between [methyl acetate], [water], [methyl iodide], [iridium], CO partial pressure, temperature and the promoter package used. For example, the methyl iodide concentration, above a low threshold value, has only a small influence on the reaction rate under certain conditions. However, when the reaction rate is declining with reducing water concentration, as shown for a ruthenium-promoted iridium catalyst in Figure 3,
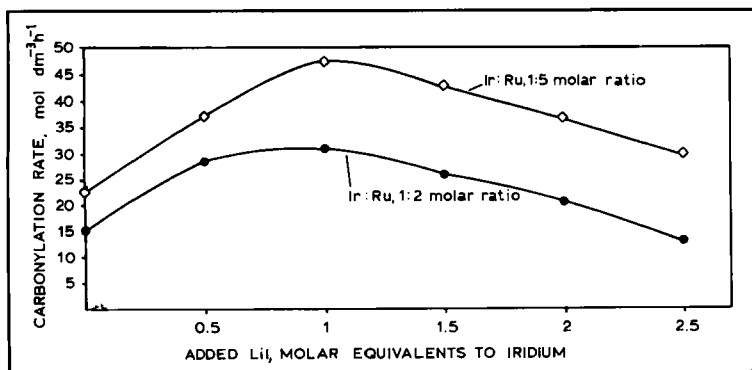

Fig. 5 The effect of adding a second promoter of lithium iodide to ruthenium-promoted iridium catalysts on the methanol carbonylation rates. Batch autoclave data taken at 2 % w/w water and 30 % w/w methyl acetate

increasing the methyl iodide concentration from 8.4 to 12.6 % w/w doubles the reaction rate. Increasing the methyl iodide concentration under these conditions also increases the effectiveness of the ruthenium promoter (16). In the Cativa™ process these interactions are optimised to maximise reactor productivity and reaction selectivity and minimise processing costs.

In addition to the batch autoclave studies, a pilot plant unit operating under steady state conditions was used to optimise the Cativa™ process. The unit provided data on the carbonylation rate, the byproducts, catalyst stability, corrosion rates and product quality under continuous steady state operation.

Purification

The quality of the acetic acid produced in the Cativa™ process is exceptional. It is inherently low in organic iodide impurities, which trouble other low water, rhodium-based, processes (14). Acetaldehyde is responsible for the formation of the higher organic iodide compounds via a series of condensation steps and other reactions. These higher iodides are difficult to remove by conventional distillation techniques and further treatment steps are sometimes necessary to ensure that the acetic acid is pure enough for all end uses.

In particular ethylene-based vinyl acetate manufacturers or those using palladium catalysts require the iodide concentration in the acetic acid to be at a low ppb level (14). In the Cativa™ process the levels of acetaldehyde in the reactor are very low, typically less than 30 ppm, compared to a few hundred ppm in the conventional Monsanto process and several hundred ppm in the lithium-promoted rhodium process. Further treatment steps are not therefore necessary to give a product that can be used directly in the manufacture of vinyl acetate.

The levels of propionic acid in the acetic acid from the Cativa™ process are substantially less than those from the rhodium process. In the conventional high water content rhodium process, the propionic acid present in the acetic acid product prior to the "Heavies" removal column is between 1200 and 2000 ppm. In the Cativa™ process these concentrations are reduced to about one third of these levels.

The Environmental Impact of Cativa™

As the Cativa™ process produces substantially lower amounts of propionic acid compared to the rhodium process, much less energy is required to purify the product. As mentioned previously, the Cativa™ system can be operated at much lower water concentrations, thus reducing the amount of energy required to dry the product in the distillation train. Steam and cooling water requirements are reduced by 30 per cent compared to the rhodium system. The water gas shift reaction does occur with Cativa™, as with rhodium, but at a lower rate, resulting in ~ 70 per cent lower direct CO_2 emissions. Overall, including indirect CO_2 emissions, the Cativa™ process releases about 30 per cent less CO_2 per tonne of product than does the rhodium process. The comparative insensitivity of the system to the partial pressure of CO allows operation with lower reactor vent rates than in the rhodium system. This results in the combined benefits of less purge gas released to the atmosphere via the flare system and also greater CO utilisation, leading to decreased variable costs. In practice, total direct gaseous emissions can be reduced by much more than 50 per cent.

Cost Reductions

As discussed before there are a number of factors which have lead to substantial variable cost reductions for the Cativa™ process compared to the rhodium process. In particular, steam usage is reduced by 30 per cent, while CO utilisation is increased from ~ 85 per cent to > 94 per cent.

The Cativa™ process also allows simplification of the production plant, which reduces the cost of a new core acetic acid plant by ~ 30 per cent. As the Cativa™ catalyst system remains stable down to very low water concentrations, the purification system can be reconfigured to remove one of the distillation columns completely and to combine the light ends and drying columns into a single column. The lower production rates of higher acids,
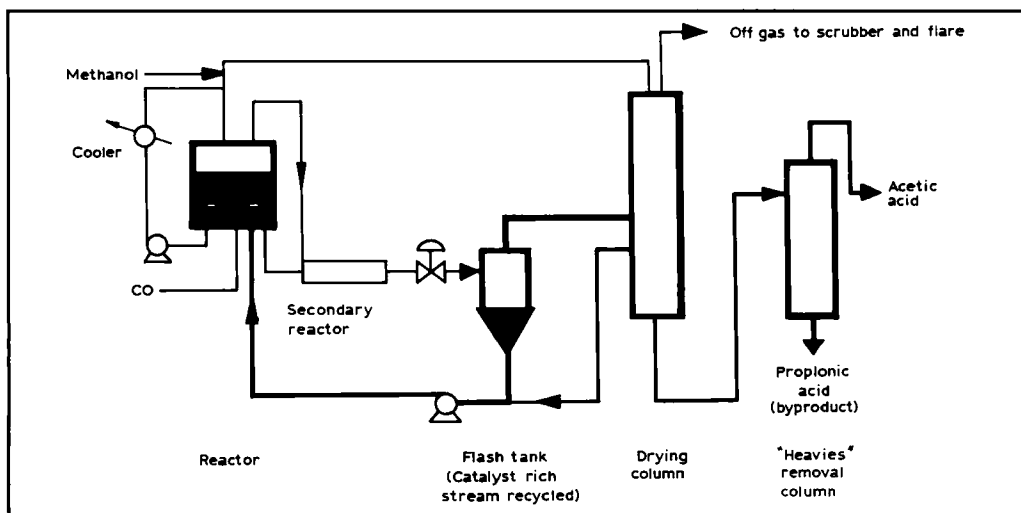
Fig. 6 Simplified process flowsheet for a commercial scale Cativa™ methanol carbonylation plant. The low boiler and water removal duties are combined into one, smaller, distillation column. The size of the high boiler removal column has also been reduced

compared to the Monsanto process, allows the size and operating cost of the final distillation column to be reduced. The major units of a commercial scale Cativa™ methanol carbonylation plant are shown in Figure 6.

The reactor in the Cativa™ system does not require a traditional agitator to stir the reactor contents. Eliminating this leads to further operational and maintenance cost savings. The reactor contents are mixed by the jet mixing effect provided by the reactor cooling loop, in which material leaves the base of the reactor and passes through a cooler before being returned to the top of the reactor. A secondary reactor after the main reactor and before the flash tank further increases CO utilisation by providing extra residence time under plug flow conditions for residual CO to react and form acetic acid.

Conclusions

The new Cativa™ iridium-based system delivers many benefits over the conventional Monsanto rhodium-based methanol carbonylation process. The technology has been successfully proven on a commercial scale at three acetic acid plants worldwide having a combined annual production of 1.2 million tonnes. These benefits include:

• an inherently stable catalyst system

• less dependence on CO partial pressure

• the reactor can run with a lower vent rate, which results in a higher utilisation of CO, which can be further improved by the addition of selected promoters. These effectively remove the dependence of reaction rate on the CO partial pressure.

• plants can operate with a higher reactor productivity, and higher rates still have been demonstrated at pilot plant scale

• the production of byproduct propionic acid is reduced, leading to reduced purification costs

• the water concentration in the reactor can be reduced as the system has a high tolerance to low water conditions. As the reactor contains less water, less has to be removed in the purification stages, again reducing processing costs.

• the level of acetaldehyde in the Cativa™ process is lower than in the rhodium process, giving a fundamentally purer product. Hydrogenation of any unsaturated species present is catalysed by the iridium species, resulting in almost complete elimination of unsaturated condensation products and iodide derivatives.

Thus, the reduced environmental impact of the Cativa™ system along with the cost reductions have allowed substantial benefits to be gained from this new industrial process for the production of acetic acid.

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Footnotes

In September 1999, the Royal Society of Chemistry gave the Cativa™ process the "Clean and Efficient Chemical Processing" award in recognition of its positive environmental impact.

BP commissioned their first plant using the rhodium-based process in 1982 licensed from Monsanto and acquired the rights to this process in 1986.

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Platinum Excavation on the UG-2 Reef in South Africa

The enormous saucer-shaped Bushveld Complex in South Africa is the world's largest layered intrusion and the major world platinum resource (1). It comprises layers rich in platinum group metals (pgms): the Merensky Reef (the traditional main source of platinum), the underlying UG-2 Reef and the Platreef in the north. The Merensky Reef has become less important recently as fewer high grade mineral-bearing deposits remain near the surface (2).

In the 1970s mining was begun on the UG-2 Reef (typically 1 m thick) where it breaks through the surface (2). Recently, in the Rustenburg area at Kroondal, Aquarius Exploration began exploration work. Here the reef has two distinct layers, allowing greater mechanisation and some open-cast mining. At Kroondal the total resource is estimated at 20.4 million tonnes (t), of grade of 5.5 g t^{-1} with a life of 14 years (3). Laboratory work on drill core samples indicated that a concentrate containing the bulk of the pgms could be produced by flotation at a coarse grind. The concentrate grade was high at ~ 400 g t^{-1} but chromium content was higher than desired. A feasibility study was then undertaken with a small shaft sunk to access ore below the oxidised zone,

and Mintek executed pilot plant runs to aid design of a concentration plant. This design, unique to the platinum industry, uses a DMS (dense media separation) plant as the first step before the flotation process. The DMS upgrades the pgm-content and rejects barren waste (chromite mining technology). A single-stage rod mill is the only mill. An attritioner to treat the rougher concentrate prior to cleaning and open-circuiting of the cleaner tails enabled production of very high concentrate grade with acceptable chromium grades. Concentrate grades of over 600 g t^{-1} were predicted at a maintained recovery at over 85 per cent (4).

Each platinum mine has some unique processing, but this new process and other technologies could help to optimise pgm operations on the more accessible UG-2 deposits and aid smaller mines to exploit pgm deposits effectively.

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