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High productivity methanol carbonylation catalysis using iridium The Cativa^{TM} process for the manufacture of acetic acid

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Abstract

Methanol carbonylation to acetic acid is catalysed with high rates at low water concentrations using an iridium/iodide based catalyst. The catalyst system exhibits high stability allowing a wide range of process conditions and compositions to be accessed without catalyst precipitation. Two distinct classes of promoters have been identified for the reaction: simple iodide complexes of zinc, cadmium, mercury, indium and gallium and carbonyl complexes of tungsten, rhenium, ruthenium and osmium. The promoters exhibit a unique synergy with iodide salts, such as lithium iodide, under low water conditions. A rate maximum exists at commercially attractive low water conditions, and optimisation of the process parameters gives acetic acid with a selectivity in excess of 99% based upon methanol. The levels of liquid by-products formed are a significant improvement over that achieved with the conventional high water rhodium based catalyst system used in the Monsanto process and the quality of the product obtained under low water concentrations is exceptional. The Cativa^{TM} process has now been successfully commercialised on three world scale plants. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Iridium; Methanol; Carbonylation; Acetic acid; Low water; Promoters; Cativa^{TM}

1. Introduction

The carbonylation of methanol is currently the preferred route for the industrial manufacture of acetic acid and accounts for approximately 60% of world acetic acid manufacturing capacity. The first process for the carbonylation of methanol to acetic acid, commercialised by BASF in 1960, used a cobalt catalyst and iodide co-catalyst and operated at high temperatures (250°C) and pressures (680 bar) [1,2]. The selectivity to acetic acid of the BASF process is about 90% based upon methanol. In 1966, Monsanto discovered that rhodium, again with an iodide co-catalyst, was a highly selective (>99% based upon methanol) catalyst for the carbonylation of methanol to acetic acid under relatively mild conditions (30–60 bar pressure and 150–200°C) [3–5]. Since its commercialisation at Texas City in 1970, the Monsanto process has been the basis of most new acetic acid manufacturing capacity. The exclusive licensing rights to the Monsanto process were acquired by BP Chemicals in 1986. In 1996, BP Chemicals announced a new methanol carbonylation process, named Cativa^{TM}, based upon a promoted iridium/iodide catalyst [6,7]. Cativa offers significant improvements over conventional rhodium based technology, namely improved catalyst stability, allowing operation at low water concentrations, high reaction rates, reduced formation of liquid by-products and improved yield on carbon monoxide. The new process was first commercialised in November 1995, where it was used to achieve a 20% debottleneck at the Sterling Chemicals' acetic acid plant in Texas City, USA.

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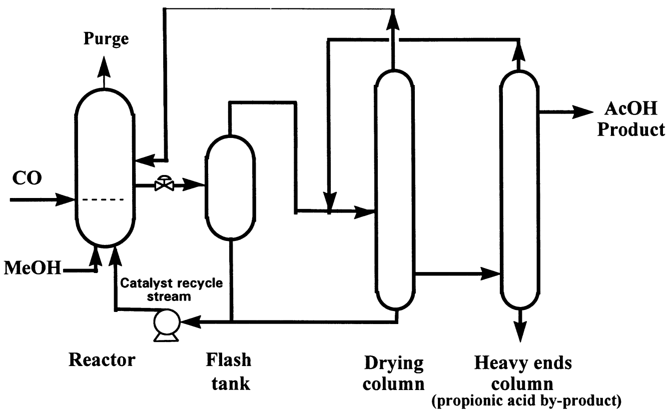


Scheme 1. Simplified process flow sheet for an acetic acid plant.

More recently the technology has been used to debottleneck Samsung-BPs' plant in Ulsan, South Korea, and BP Chemicals' plant in Hull, UK.

2. Monsanto process

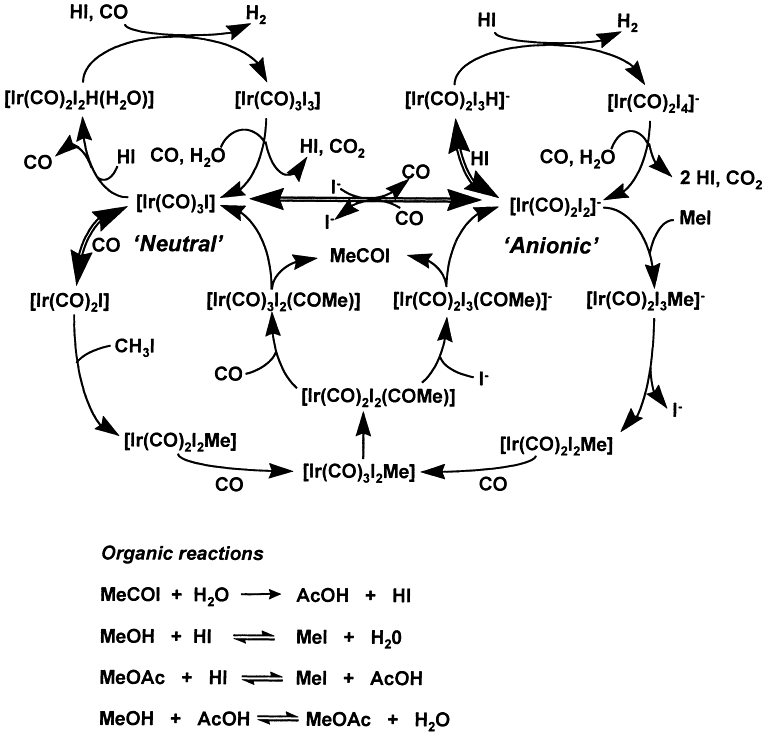
A diagram of the major units which comprise a commercial scale methanol carbonylation plant as configured for Cativa is shown in Scheme 1. Operational aspects and modifications of the Monsanto process have been reviewed elsewhere and will not be covered in detail here [8].

One of the key features of the original Monsanto process is that the conditions in the reactor have to be maintained within certain limits to prevent precipitation of the expensive rhodium catalyst in downstream areas of the plant. In these areas the catalyst is separated from the product in a CO deficient zone, the flashtank, and recycled to the reactor. To prevent rhodium loss, the reactor composition is maintained within limits on water, methyl acetate, methyl iodide and rhodium concentrations. A minimum carbon monoxide partial pressure is also required. In particular to prevent catalyst precipitation and achieve high reaction rates, high water concentrations have to be maintained. These restrictions place a limit on plant productivity and increase operating costs since the distillation section of the plant has to remove a considerable amount of water from the acetic acid product for recycling to the reactor. Significant capital and operational costs are also incurred in the necessity to operate a large distillation column to remove low levels of high boiling point impurities, the major component of which is propionic acid. Again the capacity of this column limits plant productivity.

As the Cativa catalyst remains stable down to very low water concentrations, this enables the reconfiguration of the purification system to remove one of the distillation columns completely and to decrease the size of the remaining drying column. The low production rate of higher acids compared to the Monsanto process allows for a reduction in size and operating cost of the final distillation column.

3. Iridium as a methanol carbonylation catalyst

The efficacy of iridium, with an iodide co-catalyst, as a catalyst for methanol carbonylation at low pressure was first demonstrated by Paulik and Roth [3] at Monsanto at the same time as their discovery of the well-known rhodium/iodide catalyst. At that time Monsanto chose to develop and commercialise the rhodium based catalyst system. Forster [9], at Monsanto, and others [10–12] have studied the reactivity and mechanism of the iridium based catalyst system. In the classic study of Forster [9,13,14] conducted in either methyl acetate or nonanoic acid as solvent, the mechanism of the iridium catalysed reaction was shown to be more complex than that found for rhodium. For the iridium catalysed part of the reaction two catalytic cycles were found to exist, one involving neutral catalytic intermediates, the other



Scheme 2. Forster's mechanism for iridium catalysed methanol carbonylation [9].

involving predominantly anionic species, Scheme 2. Two related cycles were also proposed for the water gas shift reaction.

In Forster's study the reaction rates reported, though reasonable, were not distinguished from those observed with rhodium. In certain regimes, e.g. at low CO partial pressure and low MeI:iridium ratios in the presence of added ionic iodide, methane and CO_2 formation was found to be considerable, resulting in a significant loss in selectivity based upon methanol and carbon monoxide.

4. Model studies

During the development of the Cativa process, to compliment our own in situ spectroscopic studies on the catalyst system, mechanistic aspects of rhodium and iridium catalysed methanol carbonylation were studied in detail by Maitlis, Haynes and co-workers, in conjunction with BP Chemicals. These studies have been used to model and quantify the differences between the two metals at the molecular level [15]. In these studies the rate of oxidative addition to $[M(CO)_2I_2]^-$ $\{M{=}Rh \text{ or } Ir\}$ was found to be 120 times faster to iridium than to rhodium at 25°C in *aprotic* solvents. In contrast, the rate of the subsequent migratory insertion reaction, again determined in aprotic solvents, was estimated to be 10^5 times faster for rhodium than for iridium at 100°C. Although the solvents used, the reaction conditions and the counter-ion employed are markedly different from those used in actual catalysis, the model studies do illustrate some of the key differences between the two metals, albeit exaggerated by the use of aprotic media. Industrially the catalysis is conducted in *protic* media, i.e. acetic acid, water and low levels of methanol, and hence, though the migratory insertion reaction can still be rate limiting under certain conditions, it does not place such a dramatic limit on the reaction rate as model studies in aprotic media would suggest. Indeed the model studies show that the migratory insertion reaction can be significantly accelerated by the addition of protic co-solvents, e.g. methanol [16]. Recent studies have also spectroscopically characterised the key reactive intermediate in the iridium catalytic cycle, $[Ir(CO)_3I_2Me]$, which, though proposed by Forster, was not observed. Kinetic studies show this species to be more labile towards migratory insertion than its anionic precursor, $[Ir(CO)_2I_3Me]^-$ [17].

5. Development of the Cativa^{TM} process

At BP Chemicals, in 1990, we began a search for new methanol carbonylation process which would offer significant improvements over conventional rhodium based technology, in particular a process that would operate at low water concentrations with high reaction rates and improved reaction selectivity. Our initial studies identified iridium as a suitable base for such a process [18,19]. Iridium was found to offer a significant benefit in terms of increased stability compared with rhodium. We here describe some of the key features of the Cativa process subsequently developed by BP Chemicals.

6. Experimental

6.1. Batch autoclave carbonylation experiments

Lithium iodide, methyl acetate, methyl iodide, $[\{Rh(CO)_2Cl\}_2]$, Bu_4NI, $[Re(CO)_5Cl]$, $[W(CO)_6]$, CdI_2, HgI_2, ZnI_2, GaI_3 (Aldrich), water (Aldrich HPLC grade), acetic acid (BP Chemicals), InI_3 (Aldrich or STREM) and CO (99.9%; Linde) were used as supplied. H_2IrCl_6 was obtained from Johnson Matthey as an aqueous solution. $[M(CO)_4I_2]$ (M=Ru or Os) was synthesised via reaction of $[M_3(CO)_{12}]$ (STREM) with iodine (Aldrich) in acetic acid at 180°C under carbon monoxide, 25 barg [24].

Carbonylation experiments were performed using a 300 ml Parr zirconium autoclave equipped with a magnetically driven stirrer with a gas dispersion impeller system, liquid injection facility and water fed cooling coils. A carbon monoxide supply to the autoclave was provided from a ballast vessel, feed gas being provided on demand to maintain the autoclave at constant pressure during a carbonylation experiment. The rate of carbon monoxide consumption was used to calculate the carbonylation rate, in mol dm^{-3} h^{-1}, at a particular point in a reaction run, the consumption of 1 mol of carbon monoxide together with 1 mol of methyl acetate and 1 mol of water being equivalent to the carbonylation of 1 mol of methanol. Compositions are quoted in % by weight (%, w/w). Reaction volumes used to calculate the reaction rate are based upon the cold degassed liquid volumes.

In a typical batch carbonylation experiment the catalyst H_2IrCl_6(aq), dissolved in a portion of the acetic acid(7.5 g)/water(7.5 g) liquid reactor charge, was charged to the liquid injection facility. If an additive was used this was placed in the autoclave, covered with a portion of the acetic acid charge (10 g), and the reactor sealed. The reactor was then pressure tested with nitrogen and vented. The autoclave was then flushed with carbon monoxide several times. The remaining liquid components of the reaction composition were charged to the autoclave via a liquid addition port. The autoclave was flushed with CO, pressurised with carbon monoxide, ca. 5 barg, and heated with stirring (1500 rpm) to reaction temperature. The total pressure was then raised to approximately 3 bar below the desired operating pressure by feeding carbon monoxide from the ballast vessel. Once stable at temperature the catalyst was injected using an over pressure of carbon monoxide to raise the total reactor pressure to the desired operating level, e.g. 28 barg. In this work the catalyst concentrations quoted are based upon a catalyst injection efficiency of 100%; catalyst recovery measurements show the efficiency to be greater than 90%. The reactor pressure was maintained constant (±0.5 barg) by feeding gas from the ballast vessel throughout the experiment. Gas uptake from the ballast vessel was measured using data-logging facilities throughout the course of the experiment. The reaction temperature was maintained within ±1°C of the desired reaction temperature by means of a heating mantle connected to Eurotherm control system. In addition, excess heat of reaction was removed by means of cooling coils. At the end of the reaction the ballast vessel was isolated and the reactor crash cooled by use of the cooling coils.

Rhodium catalysed reactions were conducted in a Parr 300 ml Hastelloy B2^{TM} autoclave. Experiments were performed as described above, the catalyst being injected into the reaction solution at temperature and

Table 1
Batch autoclave data: effect of CO partial pressure on rate for iridium catalysed methanol carbonylation[a]

Experiment	Total pressure (barg)	CO partial pressure (bar)	Carbonylation rate (mol dm^{-3} h^{-1})
1	40	25.5	10.1
2	28	13.5	10.4
3	22	7.5	8.2
4	18	3.5	5.3

[a] Reaction conditions: 190°C and 1500 rpm, autoclave charge: methyl acetate (648 mmol); water (943 mmol); acetic acid (1258 mmol); methyl iodide (62 mmol) and H_2IrCl_6 (1.56 mmol), carbonylation rate (mol dm^{-3} h^{-1}), measured at 50% conversion of methyl acetate.

pressure as a solution of $[\{Rh(CO)_2Cl\}_2]$ in acetic acid (15.0 g).

6.2. Continuous carbonylation experiments

Methanol carbonylation under steady state conditions was performed in a continuous pilot plant unit. The apparatus consisted of stirred tank reactor, a flashtank and two distillation columns, all constructed from zirconium. In some of the experiments combined light ends and drying distillation column was used. Full details, including schematics and operational aspects, are described elsewhere [20,26,29]. The unit was fed with commercial grade methanol. Carbon monoxide was supplied from a commercial plant or from pressure bottles to the reactor via a sparge fitted beneath the stirrer. To minimise iron ingress into the reactor the carbon monoxide was passed through a carbon filter. An ion exchange corrosion metal removal bed was operated to remove corrosion metals from a slip stream of the recycled liquid fraction from the flashtank (catalyst recycle stream) and thereby maintain the concentration of corrosion metals below 100 ppm in the liquid reaction composition. The liquid reaction composition was analysed by near infrared spectroscopy or by gas chromatography.

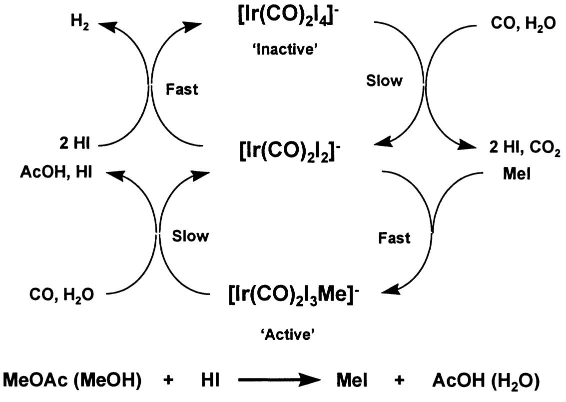
7. Results and discussion

7.1. Batch autoclave studies

Batch experiments are valuable during the development of a new process as they allow a wide range of process variables and additives to be rapidly assessed. In particular, batch experiments give a good indication of how the carbonylation rate of a continuous process will respond to changes in reaction conditions and composition. Batch studies, if interpreted carefully, also give a qualitative picture of how the reaction selectivity responds to changes in process variables. Batch experiments were conducted in acetic acid as co-solvent. The effects of key process variables and additives on the carbonylation rate are discussed below.

7.1.1. Effect of CO partial pressure

The effect of CO partial pressure on reaction rate is shown in Table 1. It can be seen that under these conditions the reaction rate drops away sharply as the CO partial pressure is reduced below approximately 10 bar. Under these conditions in situ studies, using infra-red spectroscopy to monitor the reaction in a specially designed reaction cell, show the catalyst to be operating in a regime in which the 'anionic catalytic cycle' described by Forster is predominant. The catalyst is distributed between an 'active' form, $[Ir(CO)_2I_3Me]^-$, and an 'inactive' form, $[Ir(CO)_2I_4]^-$, formed as an intermediate in the water-gas shift reaction, Scheme 3.



Scheme 3. Simplified 'anionic mechanism' for iridium catalysed methanol carbonylation.

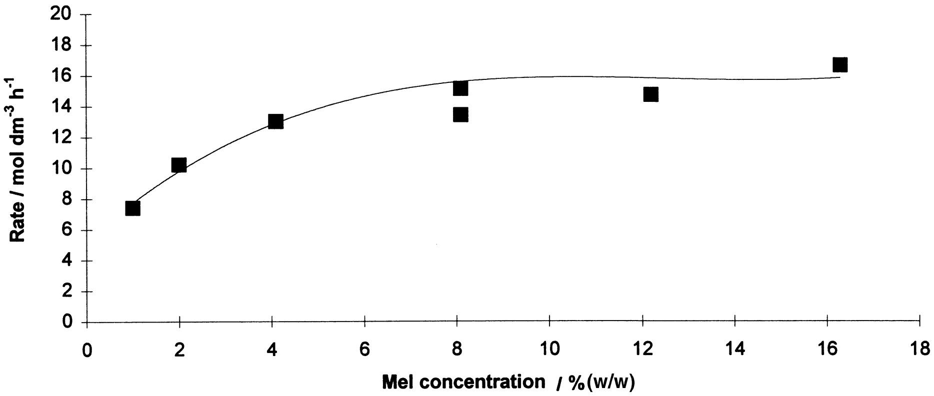


Fig. 1. Batch autoclave data: effect of MeI concentration on carbonylation rate at ca. 20% (w/w) MeOAc, 5.7% (w/w) water, 1880 ppm Ir, 28 barg total pressure and at temperature 190°C.

The reduction in reaction rate appears to be due, at least in part, to a build-up of $[Ir(CO)_2I_4]^-$ as the CO partial pressure is reduced.

7.1.2. *Effect of methyl iodide co-catalyst concentration*

Another feature of the catalyst system used in the Cativa process which distinguishes it from conventional rhodium technology is the reduced dependence of the reaction rate on the concentration of the methyl iodide co-catalyst. This is illustrated in Fig. 1 for an unpromoted iridium catalyst. The reduced dependence of the reaction rate on methyl iodide concentration compared with a rhodium system is consistent with its fast rate of oxidative addition to $[Ir(CO)_2I_2]^-$ to give $[Ir(CO)_2I_3Me]^-$.

7.1.3. *Effect of methyl acetate concentration*

The effect of MeOAc concentration on reaction rate is shown in Fig. 2. In contrast to rhodium, where the reaction rate is known to be independent of the MeOAc (and methanol) concentration across a reasonably wide range of process conditions and compositions [5], the iridium based catalyst system displays a strong rate dependence on methyl acetate concentration. High reaction rates are achievable by increasing the MeOAc

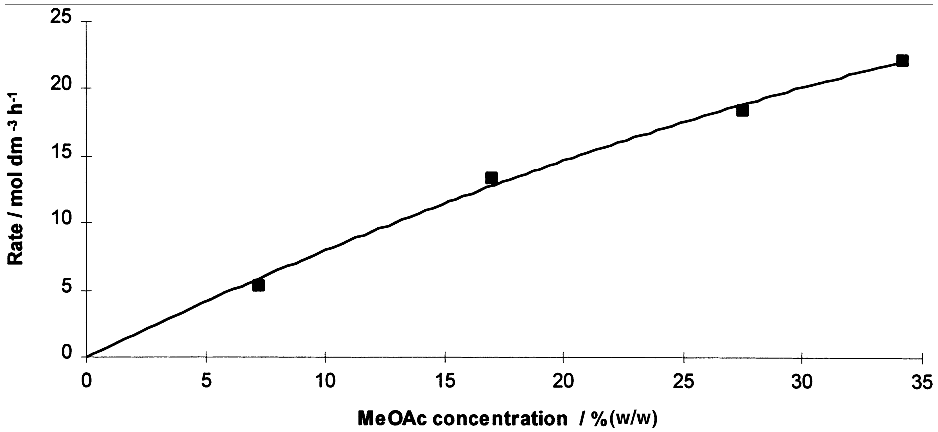


Fig. 2. Batch autoclave data: effect of methyl acetate concentration on carbonylation rate at ca. 5% (w/w) water, 8% (w/w) MeI, 1880 ppm Ir, 28 barg total pressure and at temperature 190°C.

Table 2
Batch autoclave data: effect of various additives on rate for iridium catalysed methanol carbonylation[a]

Experiment	Additive	Additive:Ir, molar ratio	Carbonylation rate (mol dm^{-3} h^{-1})
1	None	–	8.2
2	LiI	1:1	4.3
3	Bu_4NI	1:1	2.7
4	$Ru(CO)_4I_2$	5:1	21.6
5	$Os(CO)_4I_2$	5:1	18.6
6	$Re(CO)_5Cl$	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	$InI_3/Ru(CO)_4I_2$	5:1:1	19.4
14	$ZnI_2/Ru(CO)_4I_2$	5:1:1	13.1
15	$Ru(CO)_4I_2$	Control — no Ir[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_2IrCl_6 (1.56 mmol) plus additive as required, carbonylation rate (mol dm^{-3} h^{-1}), measured at 50% conversion of methyl acetate.

[b] Control experiment conducted in the absence of iridium; ruthenium complex amount used as in run 4.

[c] No CO uptake observed.

concentration significantly above that used in the original Monsanto process. In rhodium based systems such high MeOAc concentrations are not practicable in a continuous process as the catalyst would precipitate in downstream areas of the plant. In the Cativa process high MeOAc regimes are accessible owing to the high stability of the iridium catalyst on which the process is based. The positive effect of MeOAc on the reaction rate can be understood in terms of it reducing the steady state concentration of HI as its concentration is increased (via the organic reactions shown in Scheme 2). HI can have a negative impact on the carbonylation rate, as it reacts with $[Ir(CO)_2I_2]^-$ to give an 'inactive' species, $[Ir(CO)_2I_4]^-$ (Scheme 3). HI is also a source of ionic iodide which can inhibit the key migratory insertion step in the methanol carbonylation catalytic cycle as discussed below.

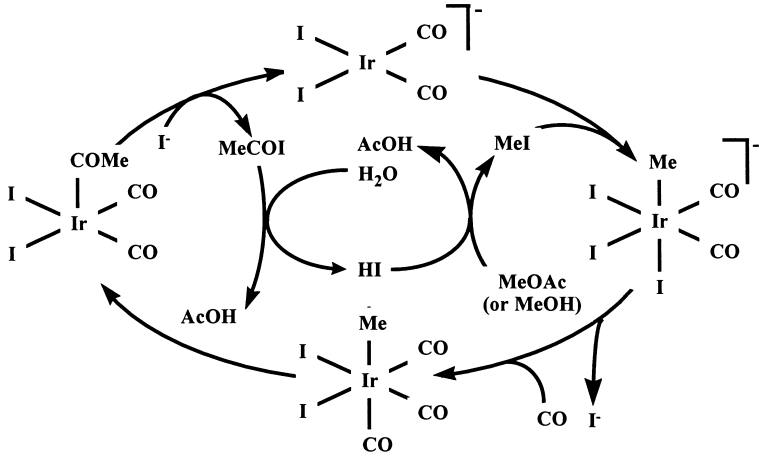
7.1.4. *Role of additives: catalyst poisons*

The effect of various additives on carbonylation rate is shown in Table 2. Both lithium iodide and Bu_4NI, are strong catalyst poisons (Table 2; runs 2 and 3), one equivalent of Bu_4NI to iridium being sufficient to reduce the reaction rate by 67%. As under these conditions, in situ studies show the 'active' form of the catalyst to be $[Ir(CO)_2I_3Me]^-$, poisoning by iodide salts is consistent with inhibition of the key migratory insertion by ionic iodide, as proposed by Forster [9]. Dissociative substitution by CO of an iodide in $[Ir(CO)_2I_3Me]^-$ is necessary to activate the complex towards migratory insertion, Scheme 4.

Iodide complexes of iron, nickel and chromium also function as catalyst poisons under these conditions and these metals, which are typically present in methanol carbonylation processes as the result of corrosion, are normally kept to a minimum in the Cativa process.

7.1.5. *Role of additives: catalyst promoters*

One of the key features of the Cativa process is the use of promoters to enhance the performance of the iridium catalyst. Work at BP Chemicals Laboratories in Sunbury on Thames and Hull identified a number of promoters which are effective across a wide range of process conditions and compositions [20–22]. In particular, the promoters are effective at promoting the reaction at low CO partial pressures. The promoters fall into two distinct groups; simple iodide complexes of zinc, cadmium, mercury, gallium and indium, and carbonyl complexes of tungsten, rhenium, ruthenium and osmium. The effect on the reaction rate of adding 5 molar equivalents of promoter to iridium is shown in Table 2. Combinations of promoters may also be



Scheme 4. Detailed ‘anionic catalytic cycle’ for methanol carbonylation using iridium.

used (Table 2; runs 13 and 14). The effect of promoter to iridium molar ratio on carbonylation rate is shown in Fig. 3 for both an indium and a ruthenium promoted catalyst. Under these conditions, by increasing the promoter to iridium molar ratio, a twofold increase in reaction rate can be achieved with indium, whilst for ruthenium a threefold increase in reaction rate is possible.

Under the relatively mild conditions employed we see no evidence for any of the promoters having any carbonylation activity prior to injection of the iridium catalyst or indeed in control experiments conducted in the absence of iridium. Ruthenium has been reported by Jenner and Bitsi [23] to be active as a catalyst for the carbonylation of methanol to methyl acetate at high pressure (450 bar at 200°C). In a control experiment (Table 2; run 15), conducted in the absence of iridium, there was no CO uptake from the ballast vessel, indicating that ruthenium on its own has negligible carbonylation activity under the conditions employed in our work. This was confirmed by GC analysis of the solution recovered from the autoclave, which showed the methyl acetate to remain unreacted, apart from a small fraction which underwent the expected hydrolysis to acetic acid and methanol (see Scheme 2).

As the promoters themselves have no detectable carbonylation activity they appear to be promoting one or more of the steps in the catalytic cycle. In

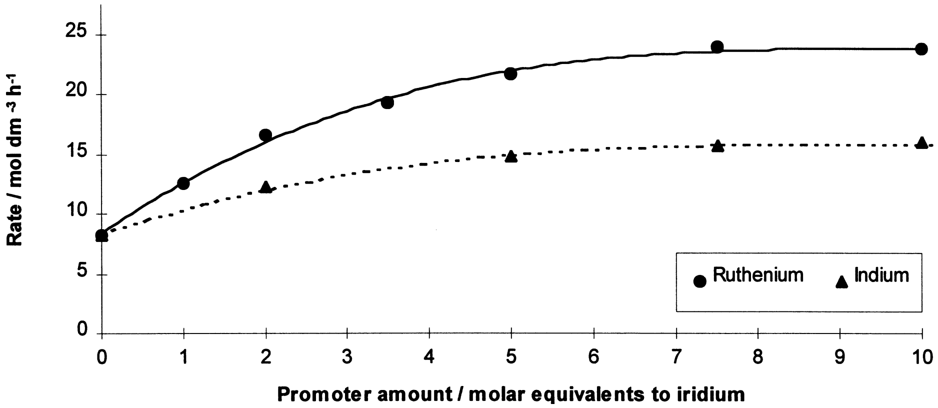


Fig. 3. Batch autoclave data: effect of promoter to iridium molar ratio on carbonylation rate at 22 barg total pressure and at temperature 190°C. Conditions as in Table 2.

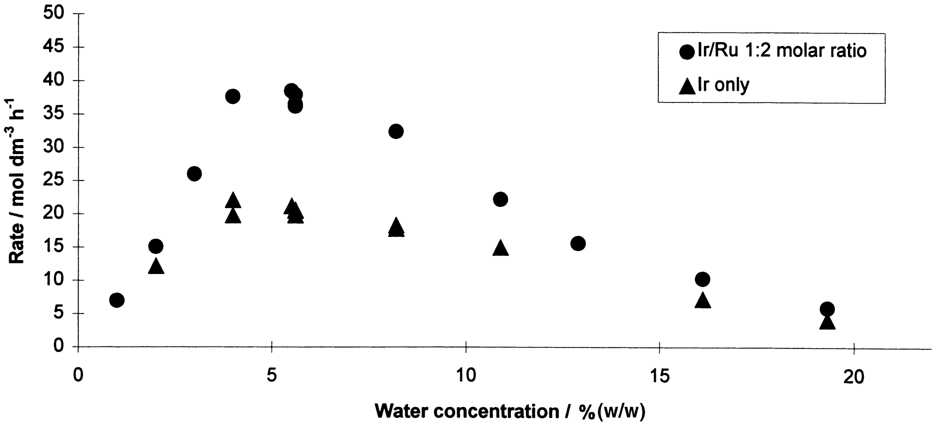


Fig. 4. Batch autoclave data: effect of water concentration on carbonylation rate at ca. 30% (w/w) MeOAc, 8.4% (w/w) MeI, 1950 ppm Ir, 28 barg total pressure and at temperature 190°C.

situ spectroscopic studies in our laboratories suggest that the promoters function by increasing the lability of $[Ir(CO)_2I_3Me]^-$ towards migratory insertion and details, including model studies conducted in collaboration with Maitlis and co-workers [24,25], will be published elsewhere. A further key role of the promoters appears to be in preventing a build-up of 'inactive' forms of the catalyst, such as $[Ir(CO)_2I_4]^-$ and $[Ir(CO)_3I_3]$, formed as intermediates in the water-gas shift reaction across a wide range of process conditions and compositions [25].

7.1.6. Effect of water concentration

A distinctive feature of the iridium based catalyst system used in Cativa is its behaviour with water concentration. As the water concentration is reduced the reaction rate increases markedly for both unpromoted and promoted iridium catalysts [26]. This is illustrated in Fig. 4 for an unpromoted iridium catalyst and for a ruthenium promoted iridium catalyst. Similar behaviour is also observed with the other promoters, e.g. zinc, as shown in Fig. 5. As the water level is reduced to low concentrations the rate reaches a maximum and then declines as very low water concentrations are approached. Fig. 4 also shows that the promoters, in this case ruthenium, are effective across a wide range of water concentrations and are most effective when the carbonylation rate approaches its maximum at low water concentrations. The position of the rate maximum with respect to water concen-

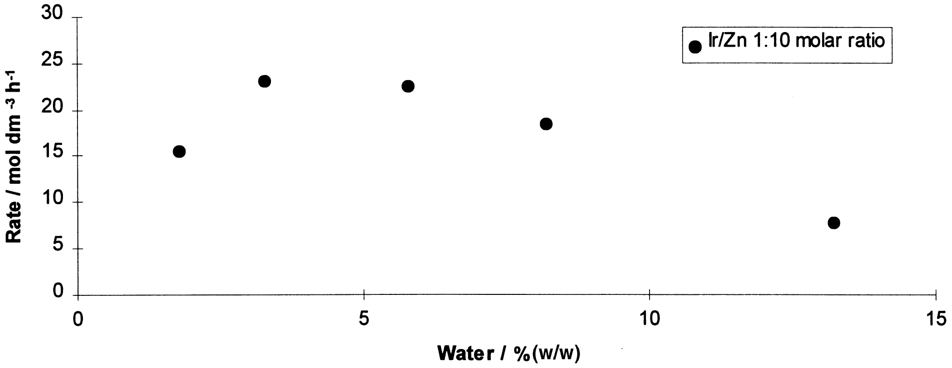


Fig. 5. Batch autoclave data: effect of water concentration on carbonylation rate at ca. 20% (w/w) MeOAc, 8% (w/w) MeI, 1840 ppm Ir, 28 barg total pressure and at temperature 190°C for a ZnI_2 promoted catalyst.

tration is a function of the other process variables, notably [MeOAc], [MeI] and CO partial pressure. In situ spectroscopic studies show the catalyst to be operating predominantly in the 'anionic catalytic regime' when the reaction rate is increasing with reducing water concentration; $[Ir(CO)_2I_3Me]^-$ and $[Ir(CO)_2I_4]^-$ are observed in the reacting solutions [25]. At very low water concentrations, when the reaction rate is declining sharply with reducing water concentration, in situ studies show the catalyst to be operating predominantly in the 'neutral catalytic regime' and $[Ir(CO)_3I]$ and $[Ir(CO)_3I_3]$ are observed in the reacting solutions [25].

As for MeOAc the effect of water concentration on the carbonylation rate can be explained in terms of its effect on the steady concentration of HI via the organic reactions shown in Scheme 2. As the water concentration is reduced the steady state concentration of HI also reduces. This has a beneficial effect on the carbonylation rate as discussed earlier for MeOAc. As very low water levels are approached there is insufficient HI to support the catalyst as an anionic species, $[Ir(CO)_2I_2]^-$ and a neutral catalytic cycle, in which MeI oxidative addition is slower and rate determining, starts to dominate. At low water concentrations the rate of reaction of the neutral 'inactive' species, $[Ir(CO)_3I_3]$, with water can also play a role in determining the overall activity of the catalyst.

7.1.7. *Role of additives: tandem promoters*

Under certain conditions a unique synergy is observed between the Cativa promoters and iodide salts and complexes, such as lithium iodide [27]. Iodide salts normally function as poisons for the iridium catalyst, as noted above. Addition of LiI to an iridium only catalyst at low water (ca. 2%, w/w) and high MeOAc (30%, w/w), when the reaction rate is declining with reducing water concentration (Fig. 4), reduces the carbonylation rate markedly (Table 3; runs 1 and 2). One molar equivalent of LiI to iridium is sufficient to reduce the reaction rate by 50%. Under the same conditions ruthenium at two molar equivalents to iridium, increases the carbonylation rate by 25% (Table 3; run 3). Remarkably, adding LiI to the ruthenium promoted catalyst under these conditions doubles the carbonylation rate (Table 3; run 4). The net effect is that ruthenium and LiI in combination increase the reaction rate by a factor of 2.5 over an unpromoted iridium catalyst. Conversely when the reaction rate is declining with increasing water concentration LiI actually poisons the ruthenium promoted catalyst [27]. Addition of low levels of iodide salts to a promoted iridium catalyst thus allows the position of the rate maximum with respect to the water concentration to be moved to lower water. The effect of LiI to iridium molar ratio on carbonylation rate is shown in Fig. 6 for a ruthenium promoted iridium catalyst, at both 1:2 and 1:5 iridium to ruthenium molar ratios. Under these conditions an exceptionally high rate of 47 $mol\,dm^{-3}\,h^{-1}$ can be achieved using a Ir:Ru:Li molar ratio of 1:5:1.

7.1.8. *Effect of catalyst concentration*

The effect of catalyst concentration is shown graphically in Fig. 7 for both an unpromoted and ruthenium promoted iridium catalyst. It can be seen that the ruthenium promoter is effective across a wide range of catalyst concentrations. Under these conditions a deviation from first-order behaviour is observed for both catalyst systems as high catalyst concentrations and high reaction rates are approached. Analysis of the liquid and gaseous by-products present at the end of the reaction indicate a small but significant loss in reaction selectivity as the catalyst concentration is increased. The production of propionic acid and its

Table 3
Batch autoclave data: effect of lithium iodide addition on rate for iridium and iridium/ruthenium catalysed methanol carbonylation at 30% (w/w) MeOAc[a]

Experiment	Catalyst system	Water (%, w/w)	Carbonylation rate ($mol\,dm^{-3}\,h^{-1}$)
1	Ir only	2.1	12.1
2	Ir/Li 1:1 molar ratio	2.0	6.3
3	Ir/Ru 1:2 molar ratio	2.0	15.1
4	Ir/Ru/Li 1:2:1 molar ratio	2.0	30.8

[a] Reaction conditions as in Fig. 4.

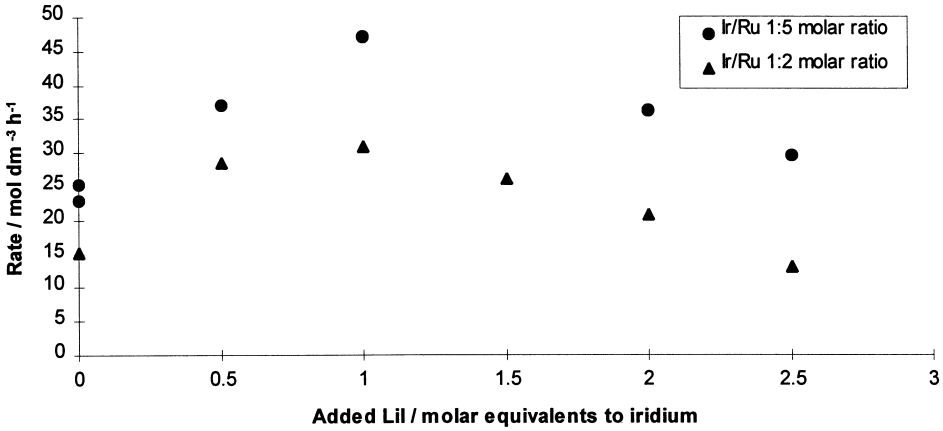


Fig. 6. Batch autoclave data: effect of lithium iodide addition on carbonylation rate for iridium/ruthenium catalysed methanol carbonylation at 2% (w/w) water and 30% (w/w) MeOAc.

precursors (ethyl iodide and ethyl acetate), methane and CO_2 all increase as the catalyst concentration is increased. Promoters, such as ruthenium, can therefore be used to increase the reaction selectivity by allowing a lower iridium catalyst concentration to be utilised to achieve a given reactor productivity [20].

7.1.9. Comparison with rhodium

A direct comparison of the conventional rhodium based catalyst with a promoted iridium catalyst is difficult as the two systems are optimised under very different conditions. In particular a comparison of the two systems in a continuous unit, using identical process conditions and compositions, is not practicable as under the high methyl acetate and low water concentrations used in the Cativa process the rhodium catalyst would rapidly precipitate in the flashtank and catalyst recycle streams. Unlike Cativa it is also necessary to operate the conventional Monsanto process at high MeI co-catalyst concentrations to achieve reasonable reaction rates. Nevertheless batch autoclave studies, in which catalyst recycle considerations are not an issue, can be instructive in comparing the behaviour of the two catalyst systems towards key process variables, in particular water concentration. A comparison of the behaviour towards water concentration of a rhodium

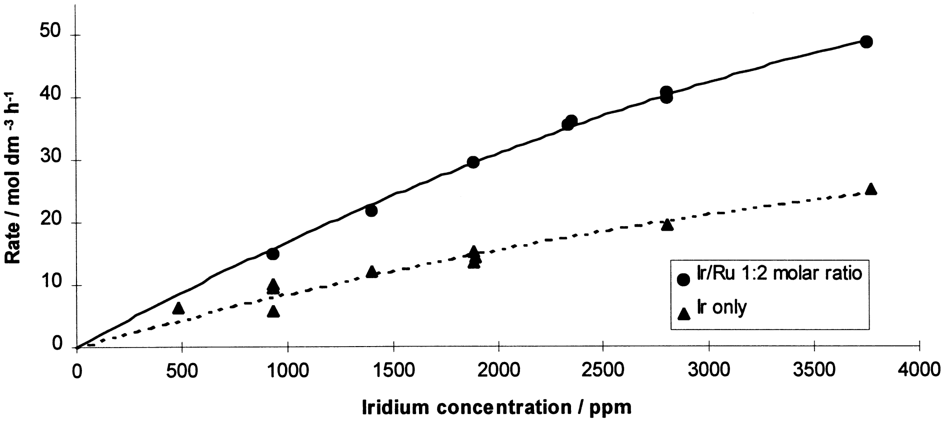


Fig. 7. Batch autoclave data: effect of iridium concentration on carbonylation rate at ca. 20% (w/w) MeOAc, 8% (w/w) MeI, 5.7% (w/w) water, 28 barg total pressure and at temperature 190°C.

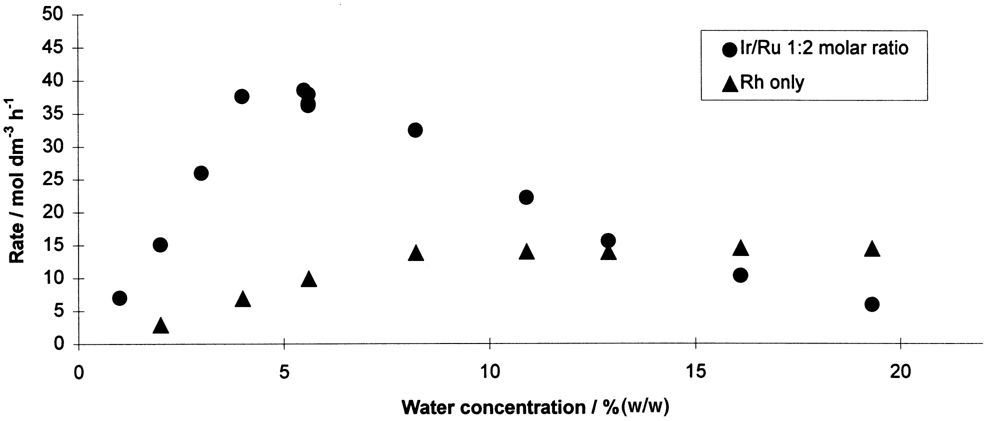


Fig. 8. Batch autoclave data: effect of water concentration on carbonylation rate for a rhodium catalyst and a ruthenium promoted iridium catalyst using equimolar amounts of rhodium and iridium. Conditions as in Fig. 4.

catalyst with a ruthenium promoted iridium catalyst is shown in Fig. 8 using equimolar amounts of rhodium and iridium. It can be seen that, at the relatively high water concentrations typical of those used in the conventional Monsanto process, that rhodium is equal or even superior in activity to a promoted iridium catalyst. At high water concentrations the carbonylation rate for the rhodium based catalyst is independent of water concentration whilst at lower water concentrations (<8%, w/w) the reaction rate starts to decline markedly with reducing water concentration [28]. By way of contrast the reaction rate for the promoted iridium catalyst increases markedly with reducing water concentration, such that at low water concentrations, for example at 4% (w/w) water, the iridium based catalyst is more than five times more active than the rhodium catalyst.

7.1.10. *Interactions of process variables*

In the Cativa process there is a complex interdependence between all the major process variables, notably between [MeOAc], [Water], [MeI], [Ir], CO partial pressure, temperature and the promoter package used. For example, the MeI concentration, above a low threshold value, has only a small influence on the carbonylation rate under certain conditions (Fig. 1). On the other hand when the reaction rate is declining with reducing water concentration, as shown for a ruthenium promoted catalyst in Fig. 4, increasing the MeI concentration from 8.4 to 12.6% (w/w) increases the reaction rate from 15 to 29 mol dm^{-3} h^{-1} at 2% (w/w) water. Increasing the MeI concentration under these conditions also increases the effectiveness of the ruthenium promoter [26]. In the Cativa process these interactions are optimised to maximise reactor productivity and reaction selectivity and minimise processing costs.

7.2. *Continuous unit studies*

A pilot plant unit, operating under steady state conditions, was used to optimise the Cativa process. This unit was used to obtain data on carbonylation rate, by-product make, catalyst stability, corrosion rates and product quality under continuous steady state operation. Selected published carbonylation rate and by-product make data are shown in Table 4 [20,26,29].

7.2.1. *Effect of iridium concentration and ruthenium addition*

In agreement with batch studies, increasing the iridium concentration from 1600 to 3240 ppm under otherwise similar conditions was not only found to increase the reaction rate from 11 to 17 mol dm^{-3} h^{-1} but also to result in a significant loss in reaction selectivity (Table 4; runs 1 and 2). The rate of CO_2 formation and propionic acid make both increase markedly upon increasing the iridium concentration. The most significant difference between the two runs is the somewhat higher CO partial pressure used, 10.0 versus 8.1 bar,

Table 4
Continuous unit data: carbonylation rate and by-product make data for iridium and iridium/ruthenium catalysed methanol carbonylation[a]

Experiment	[Ir] (ppm)	[Ru] (ppm)	Temperature (°C)	[MeI] (%, w/w)	[MeOAc] (%, w/w)	$[H_2O]$ (%, w/w)	CO partial pressure (bar)	Carbonylation rate ($mol\,dm^{-3}\,h^{-1}$)	CO_2 rate (%)	CH_4 rate (%)	Propionic acid (ppm)
1	1600	–	190.0	5.3	15.8	7.0	8.1	11.0	1.5	n.a.	530
2	3240	–	190.6	3.8	15.7	7.1	10.0	17.0	2.5	n.a.	930
3	1780	2320	190.0	5.1	15.1	7.2	8.3	17.1	1.6	n.a.	600
4	1160	1510	192.6	6.9	14.8	7.1	8.2	17.3	1.15	1.29	430
5	1180	1690	192.5	6.8	15.9	4.9	8.2	22.5	0.99	1.07	580
6	1170	1720	192.6	6.7	16.4	4.1	8.0	22.5	1.08	1.13	670
7	1130	1640	192.5	7.0	16.2	2.8	8.4	19.2	1.42	1.41	950
8	1130	1630	192.5	6.9	16.7	2.2	8.4	15.4	1.48	1.38	1150
9	840	2330	189.0	10.0	21.9	4.6	8.8	19.8	0.63	0.81	360
10	870	2870	189.0	10.3	22.3	5.7	8.3	19.8	0.67	0.84	290

[a] CH_4 and CO_2 rates quoted as a percentage of the carbonylation rate; propionic acid measured in the acetic acid product removed at the base of the drying distillation column; experiments 1, 2, 3, 9 and 10 performed on a unit with combined light ends and drying distillation column, i.e. a single column unit.

in the high rate experiment. On the other hand using a ruthenium promoter allows the reaction rate to be increased (Table 4; run 3) to 17.1 $mol\,dm^{-3}\,h^{-1}$ without a significant loss in reaction selectivity at a CO partial pressure of 8.3 bar.

7.2.2. *Effect of water concentration*

In agreement with batch studies variation of the water concentration in a series of otherwise similar experiments for a ruthenium promoted iridium catalyst shows a rate maximum at commercially attractive low conditions (Table 4; runs 4–8). Rates in excess of 20 $mol\,dm^{-3}\,h^{-1}$ are readily achievable.

7.2.3. *Reaction selectivity and CO yield*

In the Cativa process the use of promoters and optimisation of the process parameters allows acetic acid to be produced at high rates with a selectivity of greater than 99% based upon methanol. The CO_2 by-product make can also be minimised. For example runs 9 and 10 in Table 4 show both the CH_4- and CO_2-make rates to be less than 1% of the carbonylation rate. The promoted iridium process gives commercial CO yields in excess of 90% and overall yields as high as 98% can be achieved. In the conventional Monsanto process the CO yield is >85%.

7.2.4. *Catalyst stability*

A sample, containing the iridium catalyst and a ruthenium promoter, was taken from the catalyst recycle stream of the continuous unit. This was placed in a glass Fisher Porter tube under nitrogen (2 barg) and heated at 140°C for 1 h to mimic the conditions in the CO deficient areas of a plant. Visual inspection of the tube contents, both at temperature and on cooling, showed the total absence of any precipitates under the forcing conditions of this test. This was confirmed by metals analysis (by Inductively Coupled Plasma Mass Spectroscopy) of the solution before and after heating and demonstrates the inherent stability of the iridium catalyst which lies at the heart of the Cativa process.

7.2.5. *Product quality*

The levels of the liquid by-products formed in the process can also be minimised and acetic acid containing less than 400 ppm propionic acid can be produced from a unit with a combined light ends and drying column without further distillation (Table 4; runs 9 and 10) [29]. In the conventional high water Monsanto process, based upon rhodium, the propionic acid in the acetic acid product prior to the heavy ends column is of the order of 1600 ppm.

The quality of the acetic acid produced in the Cativa process is exceptional, the product being low in higher organic iodide impurities which trouble other low water, rhodium based, processes [30]. The origin of these materials is the acetaldehyde formed in the reactor via the reductive carbonylation of methanol. Acetaldehyde can undergo a series of condensation and other reactions to yield, eventually, higher organic iodide compounds. Some of these materials, especially, for example, hexyl iodide, are difficult to remove by conventional distillation and further treatment steps are sometimes necessary to give acetic acid of a quality acceptable for all end uses. Vinyl acetate manufacturers in particular require the iodide content of the acid to be at the low parts per billion level [30]. In the Cativa process the concentration of acetaldehyde in the reactor is very low, typically less 30 ppm compared to several hundred ppm in the conventional Monsanto process. Acetaldehyde is efficiently scavenged to ethyl acetate/ethyl iodide (propionic acid precursors) by the catalyst system. Consequently the level of acetaldehyde condensation products and the associated higher organic iodide containing materials formed is very low and further treatment steps are not necessary to give a product directly usable in the manufacture of vinyl acetate.

8. Commercialisation

This process is now operated commercially on three world scale acetic acid production plants. It was first introduced as part of a debottleneck of the acetic acid plant owned and operated by Sterling Chemicals at Texas City, USA in November 1995. Because of the unique combination of features of this catalyst system, i.e. giving maximum rate at very low reactor water concentration coupled with considerable reduction in side reactions, it is commercially very attractive for retro-fitting to existing production facilities.

The production capacity increase at the Sterling plant was relatively modest, being from 290 000 to 350 000 metric tonnes per year (20%). In 1997, a 75% debottleneck of the Samsung-BP acetic acid plant in Korea was commissioned. This utilises more of the features and advantages of this new catalyst system, but does not represent the full realisation of its potential. For example, reaction rates of $47\,\mathrm{mol\,dm^{-3}\,h^{-1}}$, as demonstrated in the laboratory for the iridium/ruthenium/lithium system, have not yet been commercialised.

The Cativa system has recently been installed on the BP Chemicals' acid plant at Hull, UK, again as part of a plant capacity expansion. The first purpose built Cativa plant is currently under construction in Malaysia. This is a joint venture between BP Chemicals and Petronas, and is due to start production in early 2000 with a nameplate capacity of 500 000 t per year.

9. Conclusion

The small differences in the catalytic cycles of rhodium and iridium have allowed for a surprising and novel development of what was already established as the leading process for the commercial production of acetic acid. The significantly faster oxidative addition of methyl iodide to the metal centre for iridium removes the previous rate dependence on methyl iodide concentration and allows operation with far less of this material in the reactor. At the same time, the use of a promoter package to enhance the rate of the migratory insertion reaction not only gives a higher overall reaction rate, but also significantly reduces the dependence on carbon monoxide partial pressure and hence increases the yield on carbon monoxide.

The net effect of the features of this new catalyst system is to deliver a commercially proven production process which has several benefits over the conventional Monsanto methanol carbonylation process, namely:

- higher reactor productivity;
- an inherently stable catalyst system;
- less dependence on carbon monoxide partial pressure and hence a higher yield on CO;
- lower water concentration in the reactor and hence lower processing costs;
- lower production of propionic acid by-product;
- lower acetaldehyde production and hence an inherently purer product.

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