ChemComm

Carbonylation of methanol in supercritical CO_2 catalysed by a supported rhodium complex

Rebecca J. Sowden, Murielle F. Sellin, Nicola De Blasio and David J. Cole-Hamilton*

School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland, UK KY16 9ST. E-mail: djc@st-and.ac.uk

Received (in Basel, Switzerland) 16th August 1999, Accepted 27th October 1999

A rhodium complex supported on polyvinylpyrrolidone catalyses the carbonylation of methanol to methyl ethanoate and ethanoic acid in supercritical CO_2 at rates up to *ca.* 50% those in liquid solution but with minimal catalyst leaching.

The rhodium catalysed carbonylation of methanol is an important commercial application of homogeneous catalysis in which the product can be separated from the catalyst by distillation.[1] Since this separation is carried out separately from the reaction, not all of the catalyst can be employed in the desired reaction at any one time.[1] There is, therefore, an interest in developing truly continuous processes.

One possibility would be to use a supported catalyst and to flow the reagents over it. However, in the liquid phase, catalyst leaching from the support is always a problem, although a demonstration reactor has been commissioned in which the catalyst is $[RhI_2(CO)_2]^-$ attached to an ion exchange resin. Catalyst does leach, but the dissolved catalyst is collected on a downstream bed of the resin which is recycled to the reactor.[2]

We have recently reported studies of a catalyst consisting of $[RhI_2(CO)_2]^-$ supported on polyvinylpyrrolidone (PVP).[3,4] In the liquid phase, we showed that the rate constant for the homogeneous reaction was only 2.2 times that for the heterogeneous reaction but that significant leaching of Rh occurs.[3] In the gas phase, after activation, stable activity was observed over long periods, there was no leaching, but the overall methanol consumption rate is low because of the low concentration of methanol that can be attained in the gas phase.[4]

We reasoned that supercritical CO_2 might be an ideal vector for this reaction since it dissolves large quantities of methanol and methyl iodide, is totally miscible with CO, has gas-like diffusion properties and is a poor solvent for ionic species such as $[RhI_2(CO)_2]^-$ so that leaching should be minimised. We now report preliminary results from a study of this system.

Rhodium supported on PVP was prepared as described previously[3] and tested for its activity in the bulk liquid phase. The result (Table 1, run A1) is broadly consistent with our previous results, as is the extent of rhodium leaching.[3]

The catalysts were then used for reactions in $scCO_2$. The catalyst was loaded into an autoclave with a sapphire bottom (for observation purposes). Degassed methanol and MeI were injected into the autoclave against a stream of CO_2, the autoclave sealed, pressurised to 40 bar with CO and then CO_2 added from a cooled head HPLC pump. The amount of CO_2 was varied to control the final reaction pressure which was achieved at the reaction temperature (150 °C). Observation of the catalyst shows that it changes from red to pale yellow at the onset of the reaction as indicated by a decrease in the slope of the p *vs.* T curve, which occurred between 100 and 140 °C. At the end of the reaction, the autoclave was cooled to 0 °C then to −80 °C and vented. The liquid product was removed for analysis and the autoclave recharged with methanol, MeI, CO and CO_2. We have shown, through observations on mixtures of CO_2, MeI, methanol and CO, in the absence of the catalyst, that the mixture with the same composition as that used for experiments B and C is monophasic above 130 °C. Replacing the methanol in this mixture with ethanoic acid raises the temperature at which it becomes monophasic to 150 °C, whilst a mixture in which the methanol is replaced by methyl acetate, (1.2 cm³), ethanoic acid (0.4 cm³) and water (0.4 cm³) also becomes monophasic at 150 °C.

The results of a series of runs using the same sample of catalyst are shown in Table 1 (B1–6) and Fig. 1. The rate of methanol carbonylation was *ca.* 23% that in liquid methanol, despite the fact that the concentrations of methanol and iodomethane were reduced by a factor of *ca.* 25.† Interestingly, and reproducibly, the rate increased for the second run (58% of the rate in the liquid phase) and then levelled off at a lower level for subsequent runs, despite the fact that significant amounts of Rh were leached from the support. Run B6 was carried out in the absence of added MeI; carbonylation activity was still observed at a rate similar to that observed in the previous reaction (B5). In other experiments, we have shown that the activity drops off on subsequent runs in the absence of MeI and that, if MeI is omitted from the first run in a series, no activity is observed. These results suggest that the catalyst support takes up MeI and that the rate increases as the MeI content reaches saturation either because the concentration of MeI in the supercritical phase is increased, or because the rhodium on the surface reacts with surface bound MeI (see below). When MeI is omitted from the reaction mixture, the MeI adsorbed in the surface is then used, before or after desorption, as the promoter. (Fig. 2).

In experiments B1–6, the liquid products spend significant amounts of time (up to 4 h) on the catalyst during the cooling

Table 1 Yields of carbonylation products and extent of rhodium leaching during the carbonylation of methanol catalysed by a supported rhodium catalyst under various conditions[a]

Run	MeI added/ cm³	MeOAc yield (%)	HOAc yield (%)	Turnover frequency[b]/ h⁻¹	Rh leached (%)
A1[c]	0.8	2.6	50.4	870	52.2
B1	0.3	17.0	2.2	197	12.2[d]
B2	0.3	42.2	6.9	504	11.3[d]
B3	0.3	22.8	3.4	269	6.8[d]
B4	0.3	27.0	5.6	335	3.9[d]
B5	0.3	24.5	10.5	361	12.1[d]
B6	0	33.5	4.2	383	12.4[d]
C1	0.3	20.8	1.1	178	< 0.08[e]
C2	0.3	37.5	1.3	315	0.08
C3	0.3	30.1	4.8	283	< 0.15[e]
C4	0.3	21.8	3.5	205	< 0.3[e]
C5	0.3	28.4	2.7	252	< 0.3[e]

[a] Catalyst was rhodium on polyvinylpyrrolidone (0.17 g; B, 0.82% Rh; C, 1.04% Rh); MeOH (1.5 cm³, 1.8 cm³ if no MeI added); CO (40 bar at ambient temperature); $CO_{2(l)}$ (12 cm³, 12.7 g); 150 °C; p_{150} = 200 bar, 3 h. In repetitive experiments, we have found the reproducibility is ±10%; [b] Mol of product (mol of Rh)$^{-1}$ h^{-1}. [c] Liquid phase reaction: catalyst (0.17 g, 0.82% Rh); MeOH (4.2 cm³); CO (40 bar at ambient temperature), 150 °C, 5 h. [d] From analysis of the solution recovered after each run. Analysis of the solid catalyst after the six runs indicated 39.2% of the rhodium had leached. This is less than the total of the solution figures because some of the solution and hence part of the leached rhodium remained in the autoclave after removing the condensed liquid by syringe at the end of each run. Yields of HOAc and MeOAc might be slightly overestimated for runs B2–B6 as a result of this. [e] From analysis of the solution collected in the second autoclave, detection limits for the particular experiment are shown; these correspond to < 0.3 ppm in the analyte.

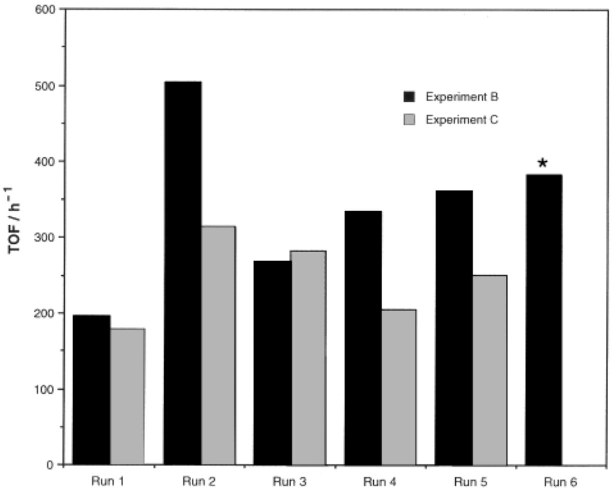

Fig. 1 Plot of turnover frequency/h^{-1} for repetitive catalytic reactions. The same catalyst was reused for all runs in a series, but different samples were used for runs B and C. For runs B, the products were condensed onto the catalyst and removed by syringe; for runs C, the products were flushed from the autoclave using $scCO_2$. The asterisk means that iodomethane was not added for this run.

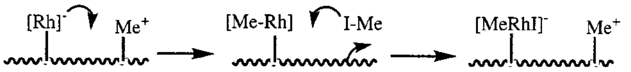

Fig. 2 Possible mechanism of reaction of the catalyst with surface bound methyl groups and remethylation of the surface.

and venting process and we surmised that the observed catalyst leaching might occur during this period of contact between the catalyst and the liquid products. To investigate the leaching under supercritical conditions, we carried out the reaction in the same way except that at the end of the reaction the stirrer was stopped and, in a process similar to that introduced by Leitner and co-workers[5] for the separation of products from homogeneous catalysts after reactions in $scCO_2$, fresh $scCO_2$ was passed into the bottom of the autoclave at the reaction temperature and pressure to flush the product solution into a second autoclave held at 40 bar and −80 °C. During this process, the CO_2 and CO were vented through an ethanol trap. The catalyst remaining in the first autoclave was reused five times (Table 1, Fig. 1, runs C1–5). The liquid product collected in the second autoclave (up to 1.2 cm^3) was analysed for the organic products by GLC and for rhodium content by atomic absorption. This series of experiments was carried out with a slightly higher catalyst loading than that for experiments B1–5, so the apparent yields are lower.‡ These lower apparent yields may arise because some solution was always left on the catalyst in the B series of experiments because the product solution was removed by syringe. This means that the starting solution for all the B series experiments, except B1, contained some product. In the C series experiments, all the product apart from that adsorbed on the support (see below) was removed by the venting process.

None of the solutions recovered after the supercritical venting process (series C) contained detectable rhodium (< 0.3% of Rh charged), apart from C2, which contained 0.08% of the rhodium charged,§ suggesting that leaching has been minimised. To confirm this, we analysed the catalyst before and after use (Table 2). The mass of the catalyst recovered was higher than that loaded, and the total rhodium content had dropped slightly (12%, although the precision of the analyses is such that this may not be significant) (see Table 2), confirming that rhodium leaching is greatly reduced when the reaction is carried out and the products are recovered in the supercritical phase.

In order to understand the increase in weight of the catalyst, we heated a sample of the recovered catalyst to constant weight in a closed system and analysed the gas phase. MeI and $MeCO_2H$ were detected by GLC and the weight loss was 22%, *cf.* 17% if all the weight gained during the catalysis were lost. In a similar experiment carried out using thermal gravimetric analysis (TGA), the weight loss in a transient process starting at 33 °C and complete by 70 °C was 13.7%. TGA was also carried out on samples of the catalyst support washed with MeI and with ethanoic acid separately. For MeI, the transient process had an onset temperature of *ca.* 30 °C and was complete at 99 °C, whilst for ethanoic acid, onset was at 22 °C and the loss was complete at 70 °C. In all the TGA experiments, substantial further weight loss occurred above 250 °C, probably from decomposition of the polymer support. The observation that MeI is held on the catalyst (even after storing for several days) supports our suggestion[4] that it interacts with the support.

Table 2 Analysis of supported catalyst used in experiments C1–5 after various treatments

	Mass of catalyst/mg	Rh content (%)	Total Rh (10^{-5} mol)
Charged[a]	170	1.04	1.7 ± 0.1
Recovered[b]	205	0.74	1.5 ± 0.1
Heated[c]	27		
Recovered[d]	21		
Expected[e]	22.4		

[a] To the reactor at the start of the series C experiments. [b] From the reactor after experiment C5. [c] Sample of catalyst taken for heating to 200 °C. [d] After heating to 200 °C, MeI and $MeCO_2H$ were released; weight loss by TGA = 13.7%. [e] If all the mass gained during the catalytic experiment were from adsorption of MeI and $MeCO_2H$.

The rates obtained in the supercritical experiments are of the same order of magnitude as those obtained in the liquid phase reactions, despite the lower concentrations of methanol and MeI in the supercritical reactions. Turnover frequencies in the gas phase reactions are comparable with those obtained in the supercritical phase (up to 595 h^{-1}, at 190 °C in the gas phase compared with up to 504 h^{-1} at 150 °C for the supercritical phase reactions). However, the gas phase reactions were carried out at a higher temperature, and the concentration of methanol achievable is very much less (1 cm^3 in 9.8 dm^3, as opposed to 1.5 cm^3 in 50 cm^3 for the supercritical reactions). Rhodium leaching is a severe problem for the bulk liquid phase reactions,[3] but is very much reduced for the reactions carried out in the supercritical or gas[4] phases.

We conclude that methanol carbonylation in the supercritical phase has the potential to overcome the problems of liquid phase (catalyst leaching) and gas phase (low methanol throughput) reactions using the same supported catalyst.

We thank the EEC for a Fellowship (M. F. S.) and support under a TMR programme and for support under the ERASMUS programme (N. De B).

Notes and references

† The supercritical reactor has a volume of 50 cm^3, whilst the liquid phase reactions were carried out in a liquid volume of 5 cm^3.

‡ Using this catalyst for an experiment under the conditions of experiment B1, we obtained a turnover frequency of 176 ± 13 h^{-1}, within experimental error the same as that obtained with the batch of catalyst used for the B experiments (197 ± 20 h^{-1}).

§ In this experiment, all of the recovered solution was used for the atomic absorption analysis, improving the detection limit for this analysis. The amount detected is at this detection limit (0.5 ppm in the analysed sample).

1 M. J. Howard, M. D. Jones, M. S. Roberts and S. A. Taylor, *Catal. Today*, 1993, **18**, 325.
2 H. Sugiyama, F. Uemura, N. Yoneda, T. Minami, T. Maejima and K. Hamato, *Jpn. Pat.*, 1997, 235250; *Chem. Abstr.*, 1997, **127**, 279841j.
3 N. De Blasio, M. R. Wright, E. Tempesti, C. Mazzocchia and D. J. Cole-Hamilton, *J. Organomet. Chem.*, 1998, **551**, 229.
4 N. De Blasio, E. Tempesti, A. Khaddouri, C. Mazzocchia and D. J. Cole-Hamilton, *J. Catal.*, 1998, **176**, 253.
5 S. Kainz, A. Brinkman, W. Leitner and A. Pfaltz, *J. Am. Chem. Soc.*, 1999, **121**, 6421 and references therein.

Communication 9/06653E