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The relative importance of heterogeneous and homogeneous methanol carbonylation using supported rhodium catalysts in the liquid phase [1]

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Abstract

Rhodium catalysts supported on ZrO_2, carbon, a cross-linked polystyrene with pendant Ph_2P groups (SDT) or polyvinylpyrrolidone have been tested as catalysts for the heterogeneous carbonylation of methanol in the bulk liquid phase. In all cases, leaching of the catalyst into solution occurs and the observed increase in the rate of production of methyl ethanoate with time is attributed to the rate of the homogeneous reaction being faster than that of the heterogeneous. A detailed kinetic analysis for the catalyst supported on polyvinylpyrrolidone suggests that the rate constant for the homogeneous reaction is ca. 2 × that of the heterogeneous at 150°C. © 1998 Elsevier Science S.A.

Keywords: Methanol; Rhodium catalyst; Kinetic analysis

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1. Introduction

The carbonylation of methanol accounts for the production of 3.5 million tons of ethanoic acid per year. The reaction is promoted by hydrogen iodide, which reacts with methanol to form iodomethane. The C–C bond forming reaction is the metal catalysed carbonylation of iodomethane to ethanoyl iodide. These organic reactions are outlined in Scheme 1. The preferred process is based on a homogeneous rhodium complex, $[Rh(CO)_2I_2]^-$ [1], although an iridium-based process has recently been commercialised [2]. A full understanding of the chemistry and advances in the process engineering involved mean that the problems usually associated with homogeneous catalysts, such as the separation of the product from the catalyst and the solvent, have been overcome and plants can be run continuously for several years without rhodium loss [1]. The process is run as a continuous batch process so that some of the catalytic mixture is removed from the reactor, the product is separated by distillation and the catalyst together with methyl iodide, methanol and water is recharged into the reactor. During the product separation phase, the rhodium complex is not taking part in the catalytic reaction so that the throughput of product per mole of rhodium is reduced from its optimum value. There is, therefore, scope for the development of a process which uses a genuine flow system and ideally this will involve a heterogeneous catalyst with the reactants and products being transported in the liquid or gas phase.

There have been many reports of the attempted development of heterogeneous catalysts for methanol carbonylation either in the liquid [3–5] or the gas [6,7] phase. In the liquid phase supports such as ion exchange resins [3,4] and polyphosphines derived from styrene divinyl benzene copolymers [5,8] have proved effective,

$$\mathrm{MeOH} + \mathrm{HI} \rightleftharpoons \mathrm{MeI} + \mathrm{H_2O}$$

$$\mathrm{MeI} + \mathrm{CO} \xrightarrow{\text{catalyst}} \mathrm{MeCOI}$$

$$\mathrm{MeCOI} + \mathrm{MeOH} \longrightarrow \mathrm{MeOAc} + \mathrm{HI}$$

$$\mathrm{MeCOI} + \mathrm{H_2O} \longrightarrow \mathrm{HOAc} + \mathrm{HI}$$

Scheme 1. Organic reactions occurring during the carbonylation of methanol.

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[1] Dedicated to Professor Peter Maitlis, a great scientist and friend.

but the similarity in rates found for the homogeneous and heterogeneous systems together with the observation of rhodium leaching [5] has led to the proposal [1] that the rhodium species is dissolved from the catalyst during the reaction and some of it is redeposited once the CO pressure is released. The working catalyst would then be identical to that used in the homogeneous systems. Attaching the rhodium complex to a carbon support via a diphosphine ligand increases the stability compared with the diphenylphosphino derived polystyrene, but deactivation still occurs [8]. In some cases, higher rates have been claimed for heterogeneous catalysts supported on quaternised or oxidised polyvinylpyridines [9], than normally observed for homogeneous systems, but direct comparisons under identical conditions were not carried out. High stability towards rhodium leaching has been claimed for rhodium supported on polyvinylpyrrolidone [10].

In this paper, we report studies aimed at evaluating the effect of different supports upon the activity and stability towards leaching of the catalyst in liquid phase batch reactions, in an attempt to identify whether a genuine heterogeneous reaction can occur under these conditions. The most promising catalyst in terms of stability and activity was then selected for a more quantitative evaluation of the relative rates of the homogeneous and heterogeneous process. Studies of the use of this catalyst in the gas-phase heterogeneous reaction will be reported separately [11], but it showed excellent stability with no apparent leaching of rhodium occurring over several tens of hours of reaction.

2. Experimental

Atomic absorption analyses were carried out by the University of St. Andrews Microanalytical Service and the Polytecnico di Milano on Pye Unicam PU9400X, fitted with a graphite furnace or PU9000 flame spectrometers. GC analyses of liquid phase products were carried out using a Philips PU4500 gas chromatograph running with JCL 6000 software and fitted with a flame ionisation detector. Nitrogen was the carrier gas and a non polar capillary column (SGE BP1) was employed. Gas phase products were analysed using a Carbosphere 80/100 mesh column in a Pye Unicam Series 204 gas chromatograph fitted with a thermal conductivity detector.

Methanol was dried by distillation from magnesium methoxide, formed in situ from magnesium turnings. Iodomethane (Aldrich) was redistilled and protected from light. Chloroform was distilled from P_2O_5 and protected from the light. All operations were carried out under dry oxygen free nitrogen using standard Schlenk line and catheter tubing techniques.

Triphenylphosphine, polymer-supported (SDT, Aldrich), polyvinyl pyrrolidone (Aldrich), $RhCl_3 \cdot 3H_2O$ (Johnson Matthey), bis(prop-2-yl)ether (Aldrich) and rhodium on carbon (1%, Engelhard) were used as received. $[Rh_2(OAc)_4 \cdot 2MeOH]$ [12], $[Rh_2Cl_2(CO)_4]$ [12] and rhodium complexes supported on zirconia were prepared by literature methods [13].

2.1. Preparation of supported catalysts

2.1.1. Rh / SDT [14]

SDT (1 g) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (0.1 g) in chloroform (125 cm^3) and the mixture stirred until the solution was colourless (48 h). The polymer was collected and washed with chloroform (2×10 cm^3) and diethyl ether (10 cm^3). The rhodium containing polymer (0.47 g) was activated by stirring in iodomethane (4.5 cm^3) in the dark for 40 min. The methyl iodide was then removed in vacuo. Atomic absorption analysis showed the rhodium content to be 2.21%. This catalyst was used in one experiment in which the conversion after 4 h was 1.5% and 19% of the rhodium had leached from the catalyst.

2.1.2. Rh / polyvinylpyrrolidone [10]

Cross-linked polyvinyl pyrrolidone (3.0 g), methanol (10 g), glacial ethanoic acid (18.8 g), iodomethane (7.5 g), water (2 g) and $[Rh_2(OAc)_4] \cdot 2MeOH$ (0.07 g) were placed in an autoclave under nitrogen and stirred at 190°C for 2 h. After cooling, the precipitate was collected by filtration and dried in vacuo. Atomic absorption analysis showed the rhodium content to be 0.72% compared with a theoretical value of 0.94% if all the rhodium had been adsorbed.

2.2. Catalytic reactions

An autoclave, fitted with a glass liner was charged with the catalyst (ca. 5 μmol of Rh, weighed and introduced in air). It was then fitted with a special head that allowed it to be used like a Schlenk tube. The autoclave was degassed with nitrogen and a mixture of methanol (4.2 cm^3) and iodomethane (0.8 cm^3) was injected in. The autoclave was pressurised to 40 bar with carbon monoxide and sealed. It was then heated to the reaction temperature using a heating band. The reaction temperature stabilised within 10–15 min. It was stirred with a magnetic stirrer generally at a rate of 350 rpm. It was shown that, although the reaction yield after short times increased with stirring speed, that at longer times decreased because catalyst was forced up the sides of the glass liner and some stuck there. After the reaction, the autoclave was cooled in a water bath for at least 1 h and the pressure slowly released. It was found that some solution had distilled into the space between the glass liner and the autoclave body. This had the same concentration of methyl ethanoate as the bulk solution. The solution was removed in air and filtered to collect the solid catalyst. Its volume was measured and it was analysed by GLC, using bis(prop-2-yl)ether as an internal standard, and atomic absorption (for Rh). The final volume of the solution was always less than 5 cm^3 (2–3.5 cm^3). Some of the losses were mechanical because of handling (1–1.5 cm^3) but some volatiles were lost during the venting process. On one occasion, the vented gases were passed through an ethanol/CO_2(s) trap. The recovered liquid (0.5 cm^3) had the same concentration of methyl ethanoate as the bulk liquid from the autoclave so that analysis of the autoclave solution is a reliable indicator of the concentration of methyl ethanoate. It cannot, however, be relied upon for quantitative analysis of the rhodium leaching.

The recovered catalyst was analysed by atomic absorption having been dissolved completely in concentrated sulphuric acid at 300°C and nitric acid (65%).

In all cases, GC analysis of the products showed, methanol, iodomethane and methyl ethanoate together with traces of 1,1-dimethoxyethane.

Reactions were checked for reproducibility and the methyl ethanoate yield was found to be reproducible within ±10%.

3. Results

Six rhodium based catalysts were prepared, three on zirconium(IV) oxide [6] with the rhodium derived from $[Rh_4(CO)_{12}]$ (1.3%, **A**; 4%, **B**) or $RhCl_3 \cdot 3H_2O$ (4%, **C**); one on carbon [7] from $RhCl_3 \cdot 3H_2O$ (1%, **D**); one on SDT, a copolymer of styrene and divinylbenzene with pendant Ph_2P units [5,8], from rhodium trichloride (2.2%, **E**) and the sixth on PVP, polyvinylpyrrolidone, [10] from rhodium(II) ethanoate (0.72%, **F**). All of these catalysts were tested in bulk liquid phase reactions for the carbonylation of methanol at 150°C and $p_{CO} = 40$ bar. The reactions were stopped after a variety of times up to 10 h and the yield of methyl ethanoate was measured by GLC. In addition, both the liquid phase and the collected solids were analysed for their rhodium content by atomic absorption spectroscopy. In order to attempt to prevent rhodium redeposition after the reaction, the autoclaves were cooled rapidly from the reaction temperature and the reaction mixtures were filtered immediately after venting the autoclaves. The major form of precipitation of rhodium in other systems is as RhI_3 [1], formed from $[Rh(CO)_2I_4]^-$, which in turn is formed from the active $[Rh(CO)_2I_2]^-$ at low p_{CO}. The rhodium(III) complexes are very dark in colour, whereas $[Rh(CO)_2I_2]^-$ is pale yellow. All the reaction solutions were pale yellow when they were filtered.

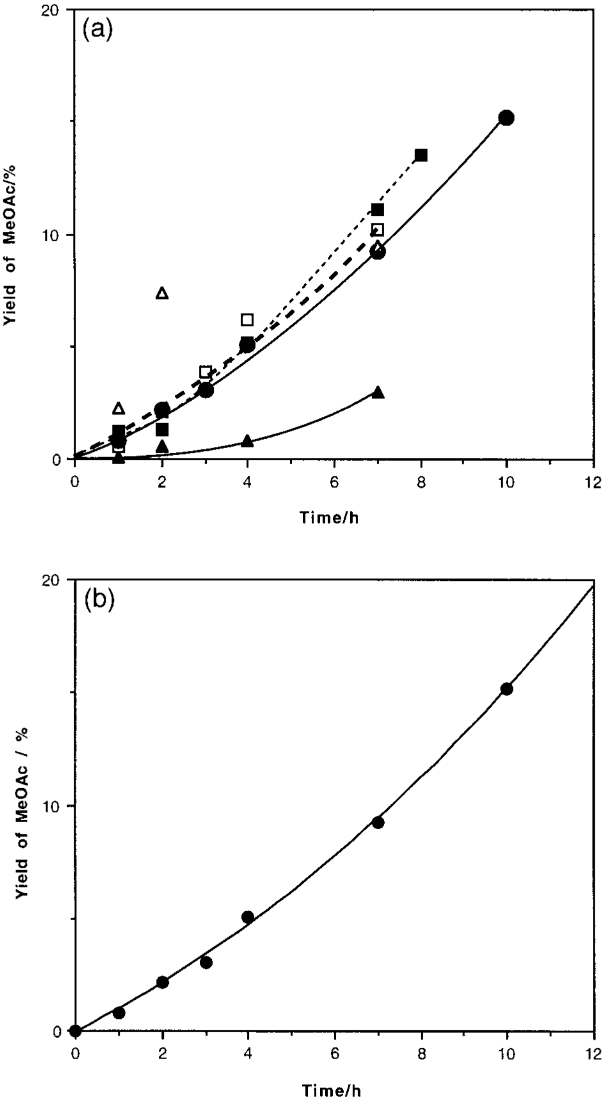

Fig. 1. (a) Plots of yield of methyl ethanoate against time for the carbonylation of methanol catalysed by **A** (– – □ – –), **B** (– – ■ – –), **C** (– ▲ –), **D** (△), and **F**(– ● –) [Rh] = 7.66×10^{-4} mol dm^{-3}). Initial [Rh] = 10^{-3} mol dm^{-3}, $p_{CO} = 40$ bar, $T = 150$°C, MeI (0.8 cm^3), MeOH (4.2 cm^3). (b) The same data replotted for catalyst **F**.

Fig. 1a shows the evolution of methyl ethanoate formation with time for five of the supported catalysts. Various trends are apparent. Thus, in almost all cases the rate of production of methyl ethanoate increases with time. This is shown more clearly for **F** in Fig. 1b. The rather unusual upward curvature of these graphs with time suggests that a more active catalyst is being produced as the reaction proceeds. [2] A comparison of catalysts **B** and **C** which differ only in the rhodium

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[2] Alternative explanations might include that the medium changes as the reaction proceeds, or that the reaction is autocatalytic (i.e., catalysed by one of the products). However, all reactions were carried out to low conversion so that changes in the medium should be minor; and there is no literature evidence for autocatalysis in the methanol carbonylation system. Furthermore, for catalyst **B**, all the catalyst leaches after ca. 4 h and in the period 4–8 h, the graph of yield of methyl ethanoate against time becomes linear. This supports our suggestion that the generally observed upward curvature arises because the leached homogeneous catalyst is more active than the supported catalyst.

precursor used to load the catalyst shows that a more active catalyst is obtained from loading with $[Rh_4(CO)_{12}]$ than with $RhCl_3 \cdot 3H_2O$. There may, however, be different effects for different supports since $RhCl_3 \cdot 3H_2O$ on carbon (**D**) shows rather high activity, although the data in this case is rather scattered. A comparison of **A** and **B**, which differ only in the rhodium loading indicates that the loading has little effect on the rate provided that the absolute amount of rhodium present is the same. The overall activities of the catalysts are broadly similar, except that **C** has rather low activity whilst **F** has the highest activity (in this case [Rh] is lower than for the other catalysts).

The extent of rhodium leaching from the catalysts determined from the concentration of rhodium in solution is presented in Fig. 2a. In all cases, extensive leaching occurs and this would account for the increase in the rate of methyl ethanoate production with time if the solubilised rhodium species more active than the supported form. Once again, the loading of the catalyst appears to have little effect upon the stability of the catalyst (**A** and **B**) and these two catalysts show very substantial leaching with all the rhodium being lost after ~ 3 h. For catalysts **C** and **D** (both loaded from $RhCl_3 \cdot 3H_2O$), the leaching is less severe than for the catalysts obtained from $[Rh_4(CO)_{12}]$ and the interaction with ZrO_2 (**C**) appears to be stronger than that with carbon (**D**). The most stable catalyst towards rhodium leaching is **F**, with only ca. 2 ppm of rhodium being observed in the solution after 2 h of reaction. This rises to 40 ppm after 10 h.

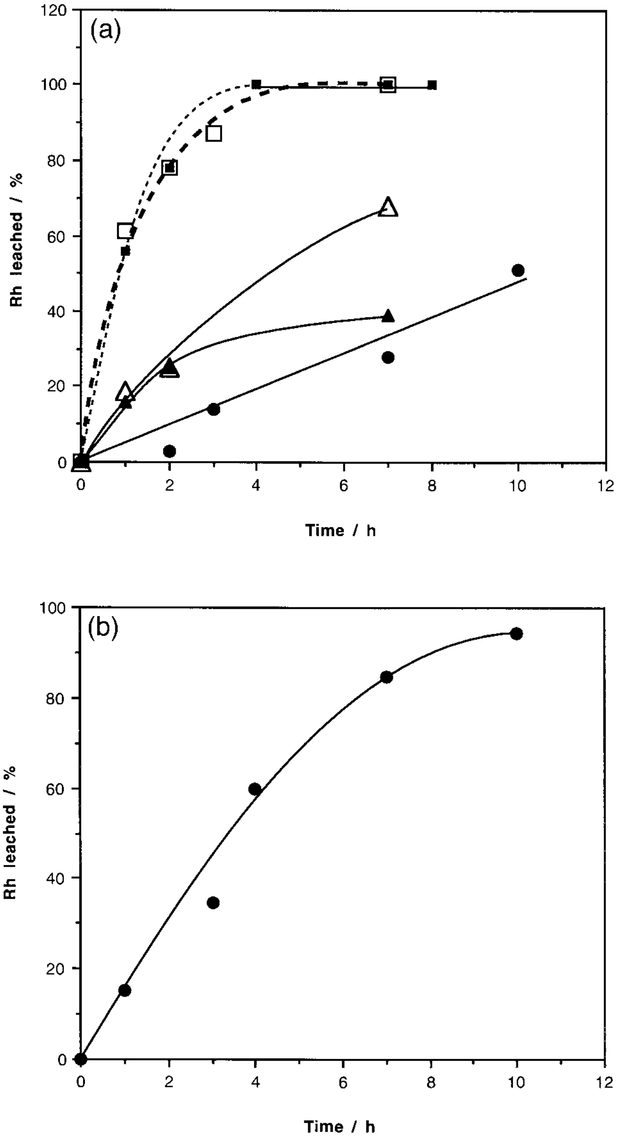

Fig. 2. (a) Extent of rhodium leaching (%) determined by measuring the solution concentration of rhodium, assuming a solution volume of 5 cm^3 for catalysts **A** (– – □ – –), **B** (– – ■ – –), **C** (– ▲ –), **D** (△), and **F** (– ● –). Conditions as for Fig. 1a. (b) Extent of leaching of rhodium determined from analysis of the recovered solid catalyst for **F**. This data was used in the kinetic analysis.

4. Kinetic analysis

The unusual shape of the graph of methyl ethanoate production against time, which we have attributed to the soluble rhodium catalyst being more active than its supported analogue, prompted us to attempt to analyse the data in more detail to try to obtain an estimate of the relative rate constants for the homogeneous and heterogeneous reactions.

The leaching process can be described by Eq. (1):

$$M_{\text{supported}} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} M_{\text{solv}} \qquad (1)$$

The overall reaction is then made up of the two processes, as exemplified in Eqs. (2) and (3):

$$2MeOH + CO \underset{M_{\text{supported}}}{\overset{k_1}{\rightarrow}} MeOAc + H_2O \qquad (2)$$

$$2MeOH + CO \underset{M_{\text{solv}}}{\overset{k_2}{\rightarrow}} MeOAc + H_2O \qquad (3)$$

Assuming that the reaction rate depends on [MeI] rather than [MeOH], as observed in the homogeneous system [1], the overall rate of production of methyl ethanoate is then given by:

$$\frac{d[MeOAc]}{dt} = k_1[MeI]^m[M_{\text{supported}}]^n[CO]^p + k_2[MeI]^q[M_{\text{solv}}]^r[CO]^s \qquad (4)$$

We can assume that [MeI] does not change during the reaction because any that is carbonylated is regenerated rapidly by Eqs. (5) and (6):

$$MeCOI + MeOH \rightarrow MeOAc + HI \qquad (5)$$

$$HI + MeOH \rightarrow MeI + H_2O \qquad (6)$$

In addition, we can assume that [CO] remains approximately constant because we are working at low conversion, but it is also known that, at least the homogeneous [1,15,16] and the gas-phase heterogeneous [17] reactions are zero order in CO for $p_{CO} > 5$ bar.

These assumptions allow us to simplify Eq. (4) to

$$\frac{d[\mathrm{MeOAc}]}{dt} = k'_1[\mathrm{M_{supported}}]^n + k'_2[\mathrm{M_{solv}}]^r \tag{7}$$

where $k'_1 = k_1[\mathrm{MeI}]^m$ and $k'_2 = k_2[\mathrm{MeI}]^q$; m and q are the orders of reaction with respect to MeI, while n and r are the orders of reaction for $\mathrm{M_{supported}}$ and $\mathrm{M_{solv}}$, respectively.

There is substantial evidence that the homogeneous methanol carbonylation reaction is first order in rhodium [1,15,16] but we can be less certain about the heterogeneous. If all the rhodium atoms are isolated in the form of supported complexes, we can expect first-order behaviour, although at high Rh loadings, two Rh atoms may be involved in the rate-determining oxidative addition of MeI [5]. If rhodium particles are present, the reaction may have an order less than 1.

We can, therefore, simplify Eq. (7) further:

$$\frac{d[\mathrm{MeOAc}]}{dt} = k'_1[\mathrm{M_{supported}}]^n + k'_2[\mathrm{M_{solv}}] \tag{8}$$

Rearranging Eq. (8),

$$\frac{d[\mathrm{MeOAc}]}{dt}\Big/[\mathrm{M_{solv}}] = k'_1\frac{[\mathrm{M_{supported}}]^n}{[\mathrm{M_{solv}}]} + k'_2 \tag{9}$$

$(d[\mathrm{MeOAc}])/(dt)$ can be determined by measuring the slope of the tangents to the graph of [MeOAc] versus time (from Fig. 1a,b). Although both $[\mathrm{M_{solv}}]$ and $[\mathrm{M_{supported}}]$ were measured, problems associated with possible evaporation of the solution during venting or while awaiting analysis suggested that the more accurate values should be those of $[\mathrm{M_{supported}}]$. These were used in the calculations with $[\mathrm{M_{solv}}]$ being obtained by subtraction of $[\mathrm{M_{supported}}]$ from the total [Rh] present during the reaction. $(d[\mathrm{MeOAc}]/dt)/[\mathrm{M_{solv}}]$ was then plotted against $[\mathrm{M_{supported}}]/[\mathrm{M_{solv}}]$. This analysis was carried out for catalyst **F** since this catalyst showed the least leaching (the rhodium leaching based on the analyses of the recovered catalysts are shown in Fig. 2b) of all of the catalysts and the highest activity for methyl ethanoate production.

Graphs were plotted for various n and that for $n = 1$ is shown in Fig. 3. The values of k'_1 and k'_2 can be calculated since k'_1 is the slope of the graph and k'_2 is the intercept. Assuming that the reaction is first order in methyl iodide and knowing its concentration (2.56 mol dm^{-3}), it is possible to calculate the heterogeneous (k_1) and homogeneous (k_2) rate constants as 0.014 and 0.031 dm^3 mol^{-1} s^{-1}, respectively. The homogeneous rate constant is then 2.2 × faster than the heterogeneous under these conditions. Straight lines are also obtained if fractional orders in rhodium are assumed for the heterogeneous reaction, so the data are insufficient to determine the order with respect to $[\mathrm{M_{supported}}]$.

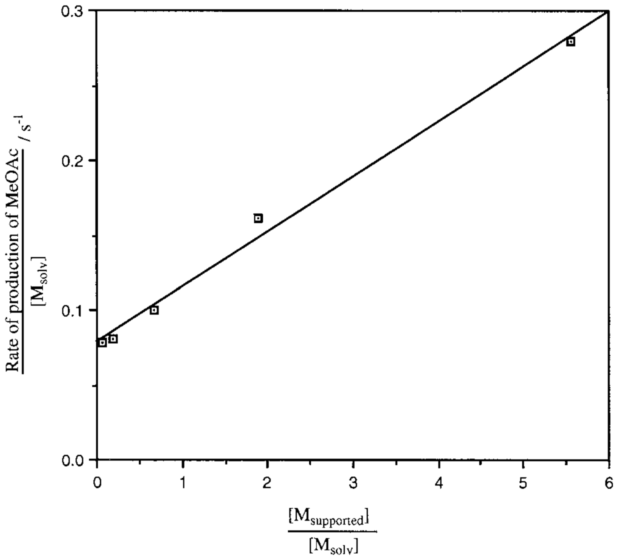

Fig. 3. Plot of rate of methyl ethanoate production/$[\mathrm{M_{solv}}]$ against $[\mathrm{M_{supported}}]/[\mathrm{M_{solv}}]$ for catalyst **F**. Conditions as for Fig. 1.

The homogeneous rate constant for the oxidative addition of iodomethane to $[\mathrm{Rh(CO)_2I_2}]^-$, the rate determining step of the catalytic reaction, has been measured both in Sheffield (0–35°C) [18] and in St. Andrews (25–80°C) [19]. Extrapolation of the values to 150°C gives k_2 as 0.015 and 0.11 dm^3 mol^{-1} s^{-1} respectively. We have also measured the rate of the carbonylation of methanol catalysed by $[\mathrm{Rh(CO)_2I_2}]^-$ at 150°C. The absolute rate is somewhat dependent upon the reactor, but the values of k_2 calculated from these measurements are in the range 0.044–0.12 dm^3 mol^{-1} s^{-1}. This compares with a value of 0.10 dm^3 mol^{-1} s^{-1} calculated from published activation parameters for the entire cycle [18]. In order to retain the heterogeneous catalyst within the solution (see Section 2.2), we have had to use rather lower stirring speeds in this study of the supported heterogeneous catalysts than in our normal studies and have shown that, at least at low reaction times the rate of the reaction depends quite markedly on the stirring rate. This perhaps accounts for the lower value of k_2 measured from the kinetic analysis presented above. Indeed, since catalyst **B** is completely leached into solution after 4 h, the reaction in the period 4–8 h using this catalyst should represent the purely homogeneous reaction under the conditions that we have used for our studies of catalyst **F**. The value of k_2 calculated for the reaction catalysed by **B** in the period 7–8 h is 0.027 dm^3 mol^{-1} s^{-1}, very close to the value of 0.031 dm^3 mol^{-1} s^{-1} calculated from the kinetic analysis of the reaction catalysed by **F**.

5. Conclusions

We conclude that all the supported rhodium complexes tested show substantial leaching of the catalyst into solution during the bulk liquid phase carbonylation of methanol. Polymer supports are more effective at preventing leaching than zirconium oxide or carbon. For rhodium on polyvinylpyrrolidone, we have provided evidence that both the heterogeneous and homogeneous forms are active with the rate constant for the homogeneous reaction being ca. 2 × that for the heterogeneous, assuming that both reactions are first order in [Rh].

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