Activity and Stability of Two Polymer-Supported Rhodium-Based Catalysts for the Vapour Phase Carbonylation of Methanol

N. De Blasio,* E. Tempesti,†,[1] A. Kaddouri,* C. Mazzocchia,* and D. J. Cole-Hamilton‡

*Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133, Milano, Italy;
†Dipartimento di Chimica e Fisica per i Materiali, Università di Brescia, Via Valotti 9, 25123, Brescia, Italy;
and ‡School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, Scotland

Rhodium catalysts supported on a diphenylphosphinated copolymer of styrene and divinylbenzene (SDT) or polyvinylpyrrolidone (PVP) have been tested as catalysts for the heterogeneous carbonylation of methanol in continuous long term vapour phase experiments under mild working conditions (P = 80 bar, T = 180–190°C). While for the SDT-supported catalyst leaching of the rhodium active species occurs, the PVP-supported catalyst, besides excellent activity and selectivity, also shows a very high stability since no detectable rhodium leaching was observed during the experiment (50 h). © 1998 Academic Press

INTRODUCTION

The rhodium-catalysed homogeneous carbonylation of methanol is a process of great industrial importance with 75% of the estimated 7 million tons per annum global acetic acid production capacity being based on this technology. In order to avoid the problems usually associated with homogeneous catalysts, such as the separation of the product from the catalyst and the solvent, there have been many reports of the attempted development of heterogeneous catalysts for methanol carbonylation either in the liquid (1–5) or the gas phase (6–9). Hardly any work can be found in the literature (10) where no rhodium losses from the catalyst are claimed.

With physically adsorbed rhodium, migration of the rhodium species occurs over the support surface (11). With chemically anchored catalysts (obtained, e.g. by classical ligand exchange reactions) the problem of rhodium leaching still persists even if the losses are reported to occur to a minor extent (2, 12).

More recently no indication for surface or vapour-phase migration of hemilabile ligands or rhodium was found for activated carbon supported catalysts (13). This has been rationalised assuming that phosphonate–phosphane hemilabile complexes are formed during the catalytic cycle which enhance the necessary formation of free coordination sites in Rh(I) intermediates by ring-opening of chelate structures, thus facilitating the generation of the more oxophilic Rh(III) intermediates by P,O-chelate formations. Activated carbon has been shown to be a suitable support for hemilabile rhodium, but normal diffusion of reactants limits the carbonylation rate over the supported catalysts.

The form of the active catalyst is uncertain and factors such as the desorption of rhodium under CO and its redeposition on release of CO pressure may at least contribute to the apparent differences between systems. Groups such as uncoordinated phosphines may quaternise under the working conditions, possibly providing a counter-ion for the $[Rh(CO)_2I_2]^-$ catalytic species. This counter-ion approach has been claimed for rhodium catalysts supported on insoluble organo-polysiloxane ammonium compounds of which $[(H_3C)N^+(CH_2CH_2CH_2SiO_{3/2})_3]_nX^{n-}$ is an example (14), where X is a rhodium-containing anion prepared from a number of precursors.

To date, convincing evidence for catalyst immobilisation under long term vapour-phase conditions is lacking. We wish to report here the results obtained with two polymeric-supported rhodium-based catalysts previously pretreated as reported by Tempesti *et al.* (15). According to their findings for the vapour phase methanol carbonylation using polymer supported catalysts, it was possible to reduce the rhodium losses by pretreating the catalysts at atmospheric pressure under the same working conditions that were then used for the carbonylation reaction. It was furthermore reported that as much as ca 50% of the rhodium originally loaded onto the support was lost due to the pretreatment, but the remaining active species was very strongly bound to the support.

EXPERIMENTAL

Atomic absorption analyses were carried out by the Politecnico di Milano Microanalytical Service on Pye Unicam PU9400X fitted with a graphite furnace or PU9000 flame spectrometers. IR spectra were recorded using a

[1] To whom correspondence should be addressed. E-mail: tempesti@bsing.ing.unibs.it.

Perkin Elmer 1710 FTIR. Polymer-supported triphenyl-phosphine (SDT, Aldrich), polyvinylpyrrolidone (PVP, Aldrich), and all other reagents were used as received. $[Rh_2(OAc)_4 \cdot 2MeOH]$ (16) and $[Rh_2Cl_2(CO)_4]$ (16) were prepared by literature methods.

PREPARATION OF SUPPORTED CATALYSTS

Rh/SDT (17). SDT (1 g) was added to a solution of $[Rh_2Cl_2(CO)_4]$ (0.2 g) in chloroform (125 cm^3) and the mixture was stirred until the solution was colourless (48 h). The precipitate was collected by filtration and dried *in vacuo*. Atomic absorption analysis showed the rhodium content to be 4.4%.

Rh/polyvinylpyrrolidone (18). Cross linked polyvinyl-pyrrolidone (3.0 g), methanol (10 g), glacial acetic 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 0.78%, compared with a theoretical value of 0.94% if all the rhodium had been adsorbed.

CATALYST PRETREATMENT

The experimental conditions chosen for the catalyst pretreatment deliberately simulated those adopted for the catalytic runs, except for the pressure. While in the former case the continuous flow system was operated at atmospheric pressure where no reaction products can significantly be detected, in the latter case the reactants contacted the catalyst at 80 bar. FTIR studies (see below) suggest that different Rh species are present at the end of the pretreatment and at the end of the catalytic runs. An atmospheric pressure continuous flow type reaction apparatus with a fixed catalyst bed was used for the pretreatment. A stainless steel tube reactor (ID = 6 mm, l = 1.4 m) was used for the activation. An accurately weighed amount of catalyst was transferred into the reactor (SDT = 3.69 g, PVP = 2.01 g). The system was heated to the desired temperature (180°C) in a nitrogen stream and the temperature was then maintained constant. Once the desired temperature was reached, a mixture of carbon monoxide and hydrogen (1/1 in volume, 200–250 ml/min) was fed to the reactor, together with a mixture of methanol and methyl iodide (5/1 in volume, 30–35 μl/min), introduced via a high-pressure syringe pump (Carlo Erba Phoenix 20). The liquid feed was vaporised in the flow system before contacting the catalyst. The effluent stream was passed through an isopropyl alcohol bubbler, cooled in an ice bath in order to condense all vapours. The catalysts were treated for a total 80 h. Atomic absorption analyses were then performed on the treated catalysts to determine the extent of the rhodium leaching.
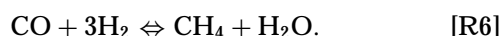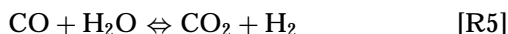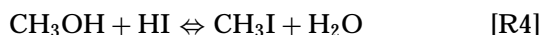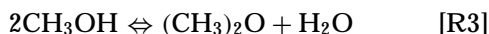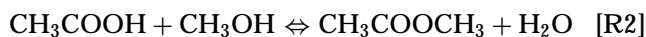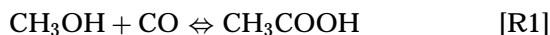
CATALYTIC TESTS

The experimental apparatus included a high pressure unit (1–100 bar) with a stainless steel tubular reactor (ID = 6 mm, l = 1.4 m), an analytical GC unit (HP 5890), equipped with capillary columns and a 10-port sampling valve, and a data logger and controller (Fluke 2280B) that operated the mass flow controllers (Brooks 5850), the sampling valve, and the reactor oven, besides safety and alarm devices. The gas stream, i.e. a carbon monoxide and hydrogen mixture (1/1 in volume), was metered with automated flow meter controllers. The pressure was measured with a pressure transducer (Schaevitz P721) and regulated by a pressure regulator. The liquid mixture of methanol and methyl iodide (5/1 in volume) was fed to the system using a high pressure syringe pump (Carlo Erba Phoenix 20). The liquid feed was vaporised in the flow system and mixed with the metered gas stream of carbon monoxide and hydrogen. Vapour phase reactants contacted the catalyst (SDT = 3.4 g, PVP = 0.78 g) at 80 bar and 180–190°C. The reaction temperature was measured and regulated by a PID Barber–Colman (Model 570) temperature controller. A metering valve was used to send an aliquot of the effluent stream to the sampling valve connected to the on-line GC. The reaction products were simultaneously analysed using two different capillary columns, an Alltech RSL 160 (ID = 0.32 mm, l = 30 m) and a Chromopack Poraplot Q (ID = 0.25 mm, l = 30 m), fitted with a FID (flame ionisation) and a TCD (thermal conductivity) detector, respectively. The rest of the product stream was cooled in order to separate all condensable components before being purged. The data logger controlled the entire system, keeping the programmed parameters constant.

RESULTS

Two rhodium-based catalysts were prepared, one supported on SDT, a copolymer of styrene and divinylbenzene with pendant Ph$_2$P units from rhodium trichloride (4.4%, **A**), and one supported on polyvinylpyrrolidone from rhodium(II) acetate (0.78%, **B**). These were pretreated under the previously reported conditions for 80 h. Atomic absorption analyses were then performed to determine if any rhodium had leached from the catalysts due to the pretreatment. These showed that for **A** ca 23% was lost, thus reducing the rhodium loading to 3.4%, while for **B** no rhodium losses had occurred. The pretreated catalysts were then tested in continuous vapour phase reactions for the carbonylation of methanol using a continuous flow reactor at the Stazione Sperimentale per i Combustibili of San Donato (Milano). For methanol conversion below 100% the acetic acid synthesis is accompanied by several other known complex equilibrium reactions [R1]–[R6]. The products observed were acetic acid [R1], methyl acetate [R2],

dimethyl ether [R3], acetaldehyde, acetaldehyde dimethyl acetal, methane [R6] and at the lowest methanol conversions traces of ethene. Methyl acetate was the major product due to esterification of the acetic acid formed with the excess methanol present. No carbonylation products were observed when only the carbon monoxide and hydrogen mixture was fed to the system:

$$CH_3OH + CO \Leftrightarrow CH_3COOH \quad [R1]$$

$$CH_3COOH + CH_3OH \Leftrightarrow CH_3COOCH_3 + H_2O \quad [R2]$$

$$2CH_3OH \Leftrightarrow (CH_3)_2O + H_2O \quad [R3]$$

$$CH_3OH + HI \Leftrightarrow CH_3I + H_2O \quad [R4]$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad [R5]$$

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O. \quad [R6]$$

At the methanol conversion levels studied the methyl iodide concentration was assumed to remain essentially constant in the reactor at the initial feed concentration (6). Although it was not possible to confirm experimentally whether the same amount of methyl iodide entered and left the reactor at any time due to the high volatility of methyl iodide, the assumption seems reasonable since the methyl iodide equilibrium reaction [R4] is extremely in favour of methyl iodide in the vapour phase reactions (6). The two catalysts were tested under the same working conditions P = 80 bar, T = 180°C, liquid feed rate (LFR) = 1.05 cm^3 (g catalyst)$^{-1}$ h^{-1}, MeOH/MeI = 5/1, gas flow rate (GFR) = 7.5 l (g catalyst)$^{-1}$ h^{-1}, CO/H$_2$ = 1/1. Typical results are shown in Table 1. A decrease in productivity from

TABLE 1

Performance Comparison of SDT and PVP Supported Catalysts for the Vapour Phase Methanol Carbonylation Reaction

	Catalyst **A**	Catalyst **B**
% Rhodium loading	3.4	0.78
Catalyst charge (g)	0.91	0.65
Productivity (g/g catalyst/h)	0.81 → 0.20	0.76
% Selectivity of oxygenated	98.4	99.4
% Methanol conversion	76	10.5

Note. P = 80 bar, T = 180°C, LFR = 1.05 cm^3 (g catalyst)$^{-1}$ h^{-1}, GFR = 7.5 l (g catalyst)$^{-1}$ h^{-1}, MeOH/MeI = 5/1, CO/H$_2$ = 1/1. Catalyst Weight; A: 0.91 g, B: 0.65 g.

23.5 to 13.3 g (g catalyst)$^{-1}$ h^{-1} (ca 43.4%) was observed for **A** as shown on Fig. 1, together with methyl acetate and acetic acid selectivities. On the contrary, **B** showed a constant productivity at 10.2 g (g Rh)$^{-1}$ h^{-1} during the entire time on-stream. The decrease in activity for **A** was ascribed to extensive leaching of the rhodium species from the support. In order to verify if any rhodium had indeed leached, an atomic absorption analysis was performed on the used catalyst. This showed that ca 30% was lost during the experiment (11 h). Thus since **B** showed a constant catalytic activity, indicating that no rhodium was being lost during the experimentation, further catalytic tests were carried out on this catalyst in order to optimise the working conditions.

The effect of the time on-stream was investigated under four different sets of working conditions (S1–S4) and it was found that, once steady-state conditions were reached, carbonylation activity remained constant within experimental
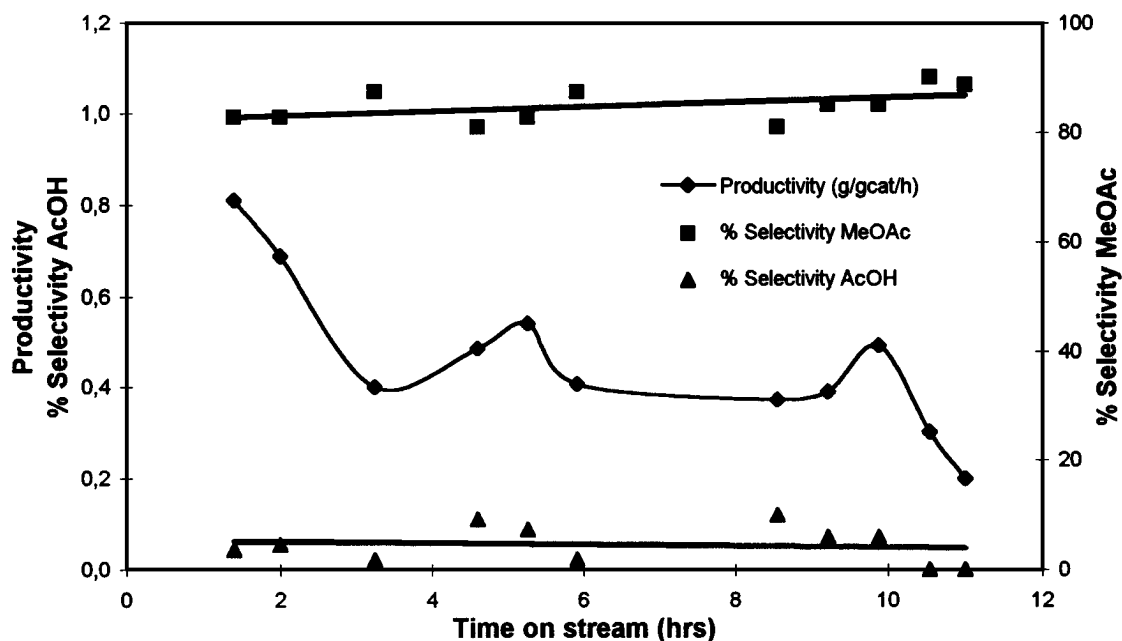

FIG. 1. Productivity (g/g catalyst/h), methyl acetate and acetic acid selectivities (%) against time using **A**.

TABLE 2

Performance of PVP-Supported Rh for the Methanol Carbonylation Reaction

	Temp. (°C)	GFR (ml/min)	LFR (ml/min)	Productivity (g/g catalyst/h)	% MeOH conversion	% Selectivity oxy.	% Selectivity MeOAc	Dimethyl ether	Acetic acid	Acetal	Ethene	Methane
S1	180	82	0.011	0.080	10.5	99.4	88.44	5.30	5.63	—	0.17	0.46
S2	180	164	0.017	0.267	34.5	99.6	88.71	7.80	1.18	1.91	—	0.42
S3	180	164	0.021	0.761	53.9	99.8	88.94	8.51	1.25	1.08	—	0.18
S4	190	164	0.021	0.900	63.4	99.8	92.45	5.81	0.48	1.09	—	0.17

Note. $P = 80$ bar, MeOH/MeI $= 5/1$, $H_2/CO = 1/1$.

error in the time range investigated. The steady-state carbonylation activities for the different sets of working conditions studied are reported in Table 2. These activities, however, are not strictly comparable since the variations in methanol conversion and productivity are due to changes in reactant concentrations and/or reaction medium rather than the variation of flow and temperature. Typical results are shown in Figs. 2–4. The best results were obtained with the last set of working conditions (S4), in which case the highest productivity (ca 0.90 g (g catalyst)$^{-1}$ h^{-1}), selectivities to oxygenated products (ca 100%), and to carbonylation products—i.e. methyl acetate (ca 93%)—were obtained. The only major by-product observed was dimethyl ether with a percentage selectivity of ca 5.8. Furthermore, since the catalyst is reported to be stable up to at least 230°C (18) we expect that, by further increasing the reaction temperature, higher productivities and methanol conversions could be obtained.

The constant carbonylation activity for **B** was a good indication that deactivation of the catalyst did not occur during the catalytic tests. In order to determine if any rhodium had indeed leached from the support an atomic absorption analysis was performed on the used catalyst (Table 3). This showed that no rhodium leaching had occurred during the experiments (ca 50 h). Therefore **B**, besides excellent activity and selectivity, showed a very high stability to rhodium losses. We attribute the higher stability of **B** with respect to **A** to a different coordination of the rhodium active species to the supports. The higher stability to rhodium leaching observed for **B** is an indication of a stronger ion-pair coordination between the rhodium species and the support (see Fig. 5). Fourier transform infrared (FTIR) transmission spectroscopy was used to verify the validity of our hypothesis (Figs. 6–7). Referring to **A** before pretreatment (Fig. 6a), the very strong band at ca 1975 cm^{-1} can be assigned to a *trans*-COClRh(PPh$_2$)$_2$ configuration, by analogy with
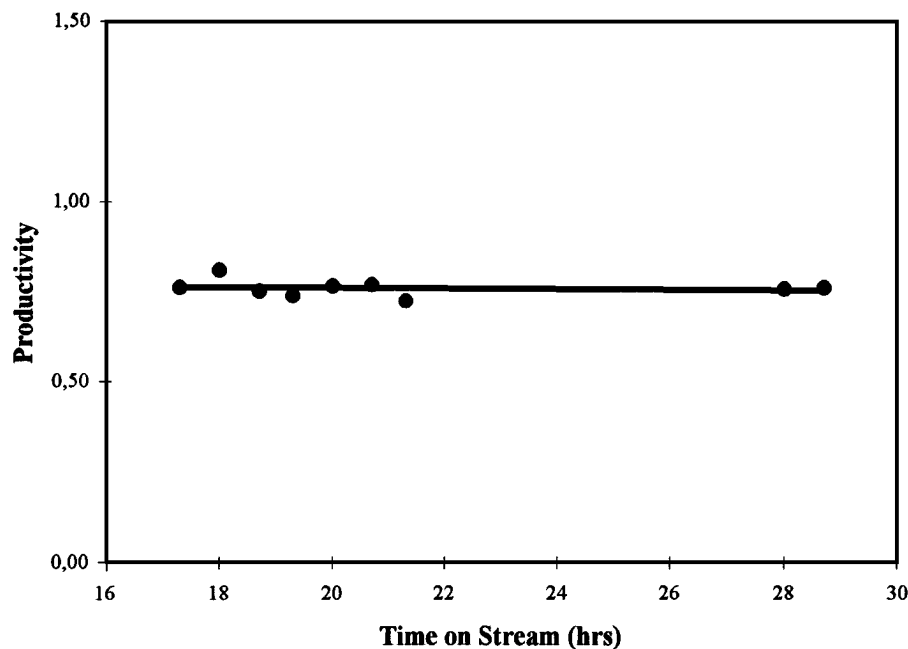

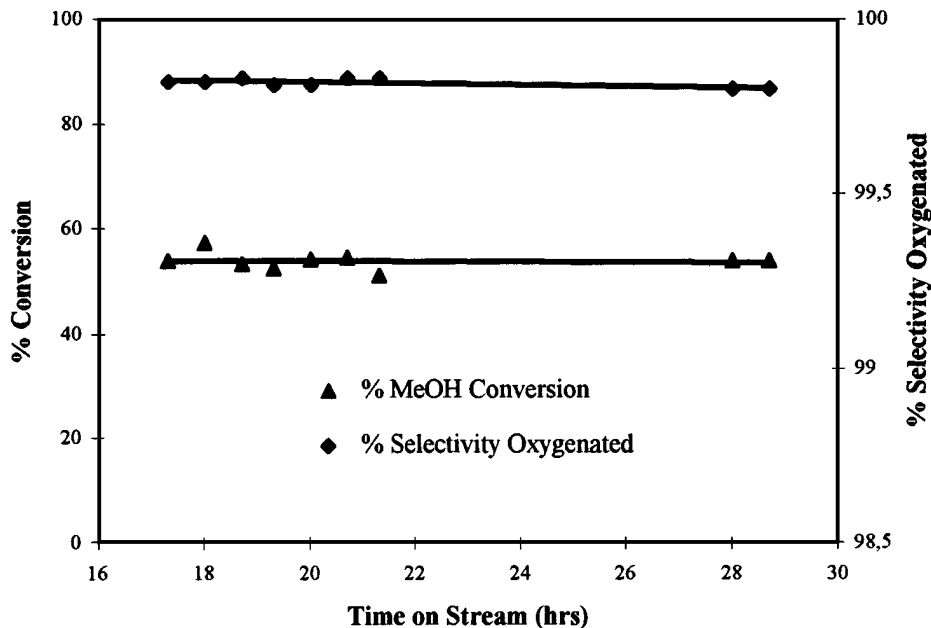FIG. 2.   Productivity (g/g catalyst/h) against time using **B**.

FIG. 3. Methanol conversion and oxygenated products selectivities (%) against time using **B**.

literature values (19–22) which is quite different from the *cis* position of carbonyls in a square planar configuration which generally shows two stretching vibrations (23). After pretreatment, there is a marked decrease in the intensity of this band, and indeed, there are no strong bands in this region (Fig. 6b). This is consistent with the atomic absorption results which show significant leaching of the rhodium, even if some rhodium clearly remains on the support, as two intense bands are observed at ca 2047 and 1976 cm^{-1} in the

FTIR spectrum after the catalytic run (Fig. 6c). These absorptions are almost identical to those from $[RhI_2(CO)_2]^-$ (24, 25), as well as to the bands obtained for **B**, which contains no phosphorus donor, after the catalytic run (Fig. 7c). It has recently been shown (22) that $[RhI(CO)(PEt_3)_2]$ is a highly active catalyst for the carbonylation of methanol under homogeneous conditions, but that it degrades rapidly to $[RhI_2(CO)_2]^-$. In the case of **A**, the counter-ions are presumably quaternised phosphonium cations. This conclusion
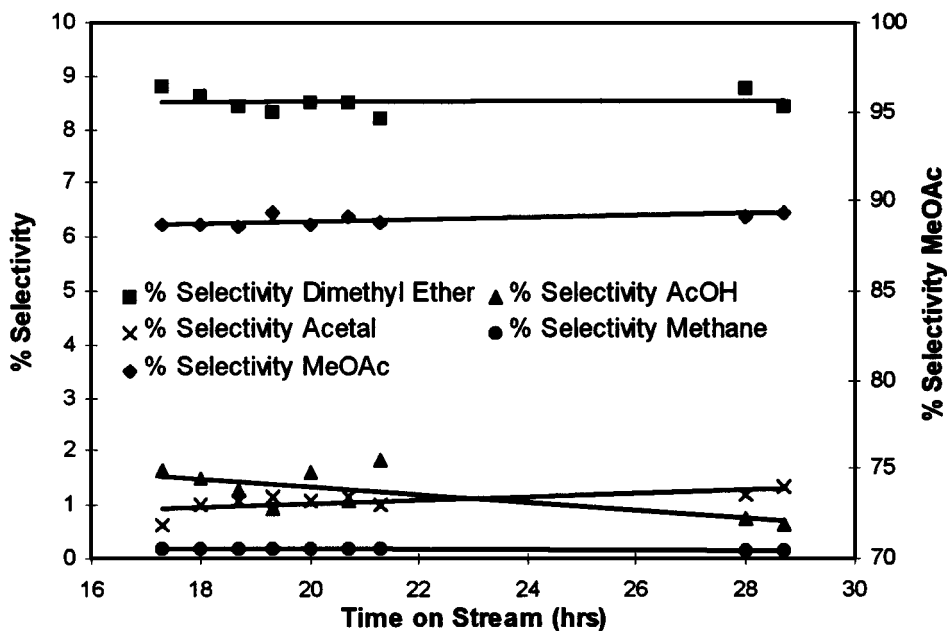

FIG. 4. Products selectivities against time using **B**.

TABLE 3

Atomic Absorption Analyses of SDT and PVP-Supported Rh Catalysts

Sample	SDT (% Rh)	PVP (% Rh)
Synthesised catalyst	4.4	0.78
Pretreated catalyst	3.4	0.78
Used catalyst	2.4	0.78

FIG. 5. Proposed active species for **B**.

is consistent with those recently reported by Mink *et al.* (26) for catalytically active complexes formed from carbon-supported $RhCl_3 \cdot 3H_2O$, carbon monoxide, and methyl iodide under relatively mild carbonylation conditions. Sample **B** shows no strong bands in this region of the IR spectrum on loading, as expected, since the starting rhodium complex contains no carbonyl ligand (Fig. 7a) nor after pretreatment (Fig. 7b). The main vibration is a broad $\nu(CO)$ from the pyrrolidone groups centred at ca 1650 cm^{-1}.

CONCLUSIONS

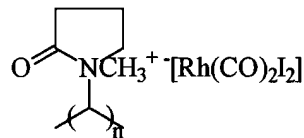The prolonged activity of a supported heterogenised catalyst for application requiring recycling or fixed-bed operation is the most important factor in its performance. Thus gradual deactivation of the catalyst by leaching of the rhodium species from the support is to be avoided to obtain an industrially viable heterogeneous catalyst for the carbonylation of methanol reaction. The polyvinyl-pyrrolidone-supported catalyst, besides excellent activity and selectivity, showed a very high stability to rhodium losses. No detectable leaching was observed after continuous long term experiments. The higher stability to rhodium losses with respect to the SDT-supported catalyst was attributed to a stronger ion-pair coordination of the rhodium species to the polymeric support. The active species has been shown to be $[RhI_2(CO)_2]^-$. To date no successful heterogeneous catalysts for the commercially important methanol carbonylation reaction have been described, while at the end of this work we can report a catalyst that showed no rhodium losses during the experiments due to
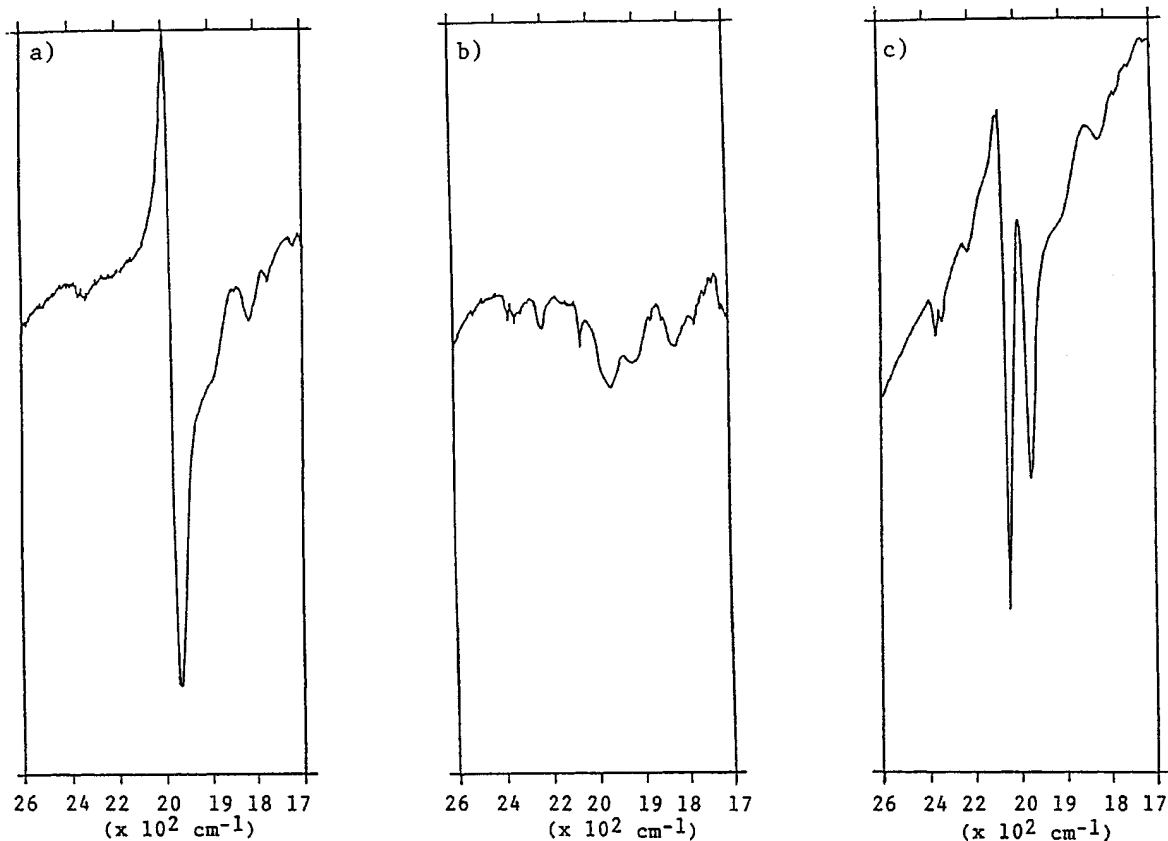

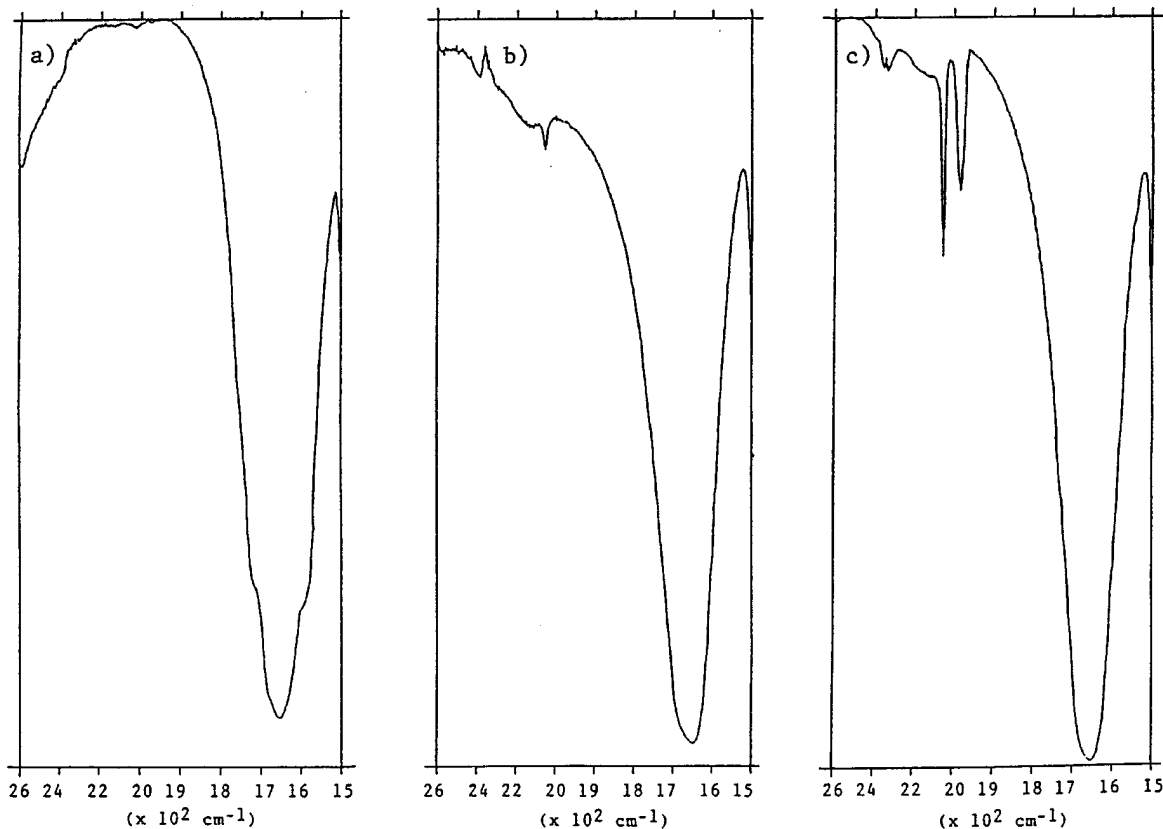FIG. 6. Infrared spectra of **A** (a) before pretreatment, (b) after pretreatment, and (c) after reaction.

FIG. 7.   Infrared spectra of **B** (a) before pretreatment, (b) after pretreatment, and (c) after reaction.

the adopted pretreating conditions which specifically affect the fixation of the active metal on the polymeric support.

REFERENCES

1. Drago, R. S., Nyberg, E. D., El A'mma, A., and Zombeck, A., *Inorg. Chem.* **20**, 641 (1981).
2. Jarrell, M. S., and Gates, B. C., *J. Catal.* **40**, 255 (1975).
3. Bartish, C. M., and Hayes, L. J., U.S. Patent 4,325,834 (1982).
4. Marston, C. R., and Goe, G. L., Eur. Patent Appl. 0,277,824 (1988).
5. De Blasio, N., Wright, M. R., Tempesti, E., Mazzocchia, C., and Cole-Hamilton, D. J., *J. Organometal. Chem.*, in press.
6. Robinson, K. K., Hershman, A., Craddock, J. H., and Roth, J. F., *J. Catal.* **27**, 389 (1972).
7. Schultz, R. G., and Montgomery, P. D., *J. Catal.* **13**, 105 (1969).
8. Tempesti, E., Kiennemann, A., Rampagnà, S., Mazzocchia, C., and Giuffrè, L., *Chem. and Ind.*, 548 (1991).
9. Krzywicki, A., and Marczewski, M., *J. Mol. Catal.* **6**, 431 (1979).
10. Howard, M. J., Jones, M. D., Roberts, M. S., and Taylor, S. A., *Catal. Today* **18**, 325 (1993).
11. Speck, J. G., and Scholten, J. J. F., *J. Mol. Catal.* **9**, 8 (1977/78).
12. Ro, K. S., and Woo, S. I., *J. Mol. Catal.* **59**, 353 (1990).
13. Bischoff, S., Weigt, A., Miebner, H., and Lucke, B., *J. Mol. Catal. A: Chem.* **107**, 339 (1996).
14. Panster, P., and Gradl, R., U.S. Patent 4,845,163 (1989).
15. Tempesti, E., Mazzocchia, C., and Kaddouri, A., Italian Patent, MI 97/A 00791 (1997).
16. Rempel, G. A., Legzdins, P., Smith, H., and Wilkinson, G., *Inorg. Synth.* **13**, 90 (1972).
17. Tempesti, E., Kiennemann, A., Ferruti, P., Chateau, L., Airoldi, G., and Mazzocchia, C., Italian Patent, MI 94/A 001277 (1994).
18. Scates, M. O., Warner, R. J., and Torrence, G. P., U.S. Patent, 5,281,359 (1994).
19. Tempesti, E., Kaddouri, A., Airoldi, G., and De Blasio, N., *J. Thermal Anal.*, in press.
20. Ro, K. S., and Woo, S. I., *J. Mol. Catal.* **59**, 353 (1990).
21. Shimazu, S., Ishibashi, Y., Miura, M., and Uematsu, T., *Appl. Catal.* **35**, 279 (1987).
22. Rankin, J., Poole, A. D., Benyei, A. C., and Cole-Hamilton, D. J., *Chem. Comm.*, 1835 (1997).
23. Terreros, P., Pastor, E., and Fierro, J. L., *J. Mol. Cat.* **53**, 359 (1989).
24. Browning, J. P., Goggin, L., Goodfellow, R. J., Norton, M. G., Rattray, A. J. M., Taylor, B. F., and Mink, J., *J. Chem. Soc. Dalton Trans.*, 2061 (1977).
25. van't Blik, H. F. J., Van Zon, J. B. A. D., Huizinga, T., Vis, J. C., Koningsberger, D. C., and Prins, R., *J. Am. Chem. Soc.* **107**, 3139 (1985).
26. Bodis, J., Zsako, J., Nemeth, Cs., and Mink, J., *Vibrational Spectroscopy* **9**, 197 (1995). See also Wang, Q., Liu, H., Han, M., Li, X., and Jiang, D., *J. Mol. Catal. A: Chem.* **118**, 145 (1997).