

Heterogenised Homogeneous Catalysts

RHODIUM CATALYSTS FOR METHANOL CARBONYLATION

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Heterogeneous versions of homogeneous catalysts can often be produced and may have certain advantages in use particularly on a commercial scale. The catalytic chemistry of supported rhodium compounds for the carbonylation of methanol is described and the behaviour of heterogeneous and homogeneous operation compared in order to illustrate the relations between the two catalyst types. Particular attention is given to the factors which influence the activity and the selectivity of the heterogenised forms.

Recently a tremendous interest has arisen concerning the behaviour of "heterogenised" forms of catalysts, such as transition metal complexes, which were previously used in homogeneous media (1). The growth of activity in this area reflects the importance which is being attached to the considerable potential offered by the new generation of catalysts. Homogeneous catalysts frequently exhibit very high activity and selectivity but their use on a large scale is often complicated by difficulties associated with their separation from the reaction products and also with problems of corrosion.

These drawbacks can in principle be overcome by binding the catalyst to a solid material, thus using the active compound in a heterogenised form. Suitable support materials which have been used include insoluble polymers (2, 3, 4) and silica (5).

The extent to which the catalytic behaviour of such heterogeneous systems parallels that displayed by the unsupported complex and the possible effects on reaction of the support itself are two obviously important factors which must be considered in the first instance. In addition, we must consider the stability of the bound catalysts and examine their operation with both liquid and vapour

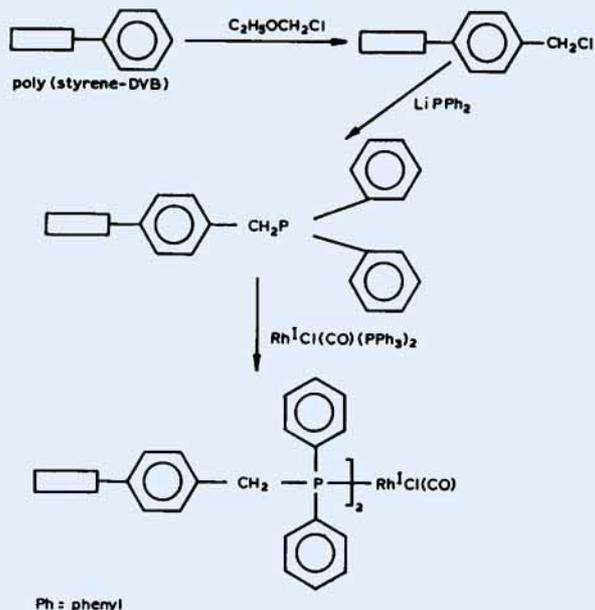
phase reactants. Our knowledge concerning these points is still fragmented, but sufficient work has now been reported to indicate that supported versions can exhibit activities and selectivities comparable with those of their homogeneous counterparts. An excellent illustration is provided by the use of rhodium catalysts in the carbonylation of methanol to acetic acid.

Carbonylation with Homogeneous Catalysts

It is helpful to consider first the behaviour of rhodium catalysts in homogeneous media. The components of the active material comprise a rhodium compound and a halogen promoter, which is preferably iodine (6, 7). The latter may be supplied as methyl iodide, hydrogen iodide, calcium iodide or iodine itself. Reaction with methanol is normally carried out (6, 7, 8) at 150 to 225°C and at a total pressure of 1 to 100 atmospheres. Selectivity for the production of acetic acid is typically about 99 per cent.

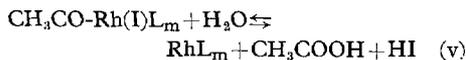
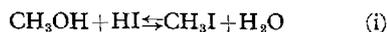
Traces of dimethyl ether and possibly acetaldehyde are produced, and this is particularly evident if the reaction is conducted using methanol itself as solvent. Acetic acid may not be recovered in all cases

Synthesis steps in the preparation of a polymer supported complex



because of esterification to methyl acetate.

The rate of carbonylation is found (7, 8) to be directly proportional to the concentrations of rhodium and iodine, but is independent of methanol concentration and carbon monoxide pressure. The suggested reaction sequence is depicted below:



Step (ii), the oxidative addition of methyl iodide to the rhodium complex is rate determining (7, 8), with the remaining steps taking place much more rapidly. Although the initial complex is denoted RhL_m , ligands of different types may be present. Roth et al (7) have demonstrated that rates of reaction and product distributions are very similar for a variety of rhodium compounds, including

RhCl_3 , Rh_2O_3 , $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ (Ph = phenyl) and $\text{Rh}(\text{CO})_2\text{Cl}_2$. Suitable solvents are low molecular weight hydrocarbons such as benzene, or one of the reactants, methanol, acetic acid, methyl acetate or water.

The catalysts have provided the basis for the development of new technologies for methanol carbonylation (7) and also for the related alkene hydroformylation process (9).

Successful though the homogeneous catalysts have proved, it is clear that heterogeneous analogues, if sufficiently active and selective, could offer considerable advantages in solving both separation and corrosion problems (10).

Heterogenised Catalysts

Several examples of methanol carbonylation by solid catalysts comprising in each case one of a range of rhodium compounds bound to a support material have been reported recently. The carriers have included carbon, alumina, poly(styrene-divinylbenzene) and a type X molecular sieve zeolite.

The polymer supported catalyst (11) was prepared by linking chlorocarbonylbis-(triphenylphosphine)rhodium, $\text{RhCl}(\text{CO})\text{-(PPh}_3)_2$ to membranes or beads of poly-(styrene-divinylbenzene). The synthesis method (3) is summarised in the Figure. Carbonylation was carried out using vapour phase reactants with the membrane or by suspending the beads in a liquid reactant mixture. Catalytic activity was associated with the presence of a Rh(I) complex. A steady conversion of rhodium from Rh(I) to Rh(III) during the reaction resulted in a fall in activity of the membrane catalyst. The activity of the catalyst in liquid medium also declined with time but in this case loss of rhodium from the support appeared to be responsible. A reduction in this loss might, it was suggested, be obtained by using a different polymer as support, or by increasing the number of coordinating groups linking the complex and support. Some dimethyl ether was produced in side reactions with these catalysts.

The mechanism suggested by Roth et al (7) for homogeneous catalysis and supported by kinetic investigations (8) also affords an explanation of the kinetics observed for the heterogenised catalysts in both liquid and vapour phase operation. The presence of an iodine based promoter is again found to be essential. One difference concerns the evidence that two adjacent rhodium centres are involved in the oxidative addition of methyl iodide for the heterogeneous catalyst rather than one as shown in the reaction sequence for homogeneous reaction.

Carbon has also been found to provide a useful support (12, 13, 14). Here too a close similarity in behaviour of heterogeneous and homogeneous catalysts is observed (14). Rhodium trichloride may be used as a starting material (14) but rhodium nitrate is preferred (12, 13). The nitrate based catalysts are more active than those prepared from such complexes as $\text{Rh}(\text{acac})_3$, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{RhCl}(\text{PPh}_3)_3$, where acac is acetylacetonate, by factors of up to 10

for operation at 200°C (13). An active material is produced by impregnation of the carbon with a solution of rhodium nitrate followed by decomposition of the latter at temperatures of 300°C and above. An increase in activity is seen on using temperatures in excess of 300°C and this appears to be associated with conversion of the nitrate to oxide. Decomposition in hydrogen rather than nitrogen resulted in a lower rate of reaction and from this evidence it might be inferred that rhodium in the reduced state or as free metal is not required. The situation remains uncertain however, since hydrogen treatment has a favourable effect on the activity of catalysts obtained from rhodium trichloride. Selectivities for carbon supported catalysts of up to 99 per cent have been reported (12).

A number of organometallic complexes of rhodium have been examined for carbonylation activity when supported on γ -alumina (15). The carrier was pre-dried at 650°C and the complexes incorporated by impregnation of the oxide with a benzene solution of the required compound. The resulting solids were active for conversion of methanol (120 to 200°C, vapour phase reactants, total pressure 1 atmosphere), but selectivity for acetate formation was in nearly every case rather low (less than 50 per cent) because of ether production. This was true of catalysts based on, for example, $\text{RhCl}(\text{PPh}_3)_3$, $(\text{codRhCl})_2$ and $(\text{codRhOCH}_3)_2$ (cod = cycloocta-1,5-diene). On the other hand those derived from $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ had about the same overall activity but were much more selective (approaching 99 per cent).

As with the work using carbon the exact state of the rhodium complex in an active catalyst remains obscure. Because different starting materials resulted in catalysts having different selectivities there is some reason to suppose that the molecular identity of the complex is retained, at least to some extent.

The rather large amounts of ether produced by most of these catalysts may very well be due to the use of alumina as the support,

Comparison of Catalyst Activities for Methanol Carbonylation			
Rates of reaction at 250°C, with $p_{CO}=1$ atmosphere and molar ratio methanol:methyl iodide=10. All reactants in the vapour phase for heterogenised catalysts.			
Catalyst	Rhodium content of catalyst, in weight per cent	Rate, expressed as g methyl acetate/g Rh/h	Reference
RhCl(CO)(PPh ₃) ₂ —alumina	1.39	40	15
Rh(NO ₃) ₃ —carbon	3	25	12
RhCl ₃ —NaX	0.25	50	17
RhCl ₃ —NaX	1.0	10	17
RhCl(CO)(P _p) ₂ *	3.6	8**	11
RhCl ₃	homogeneous catalysis	3×10^3	8

*P_p = p-(polystyryl)diphenylphosphine ligand

**Molar ratio methanol:methyl iodide typically >15

particularly since the oxide was dried at high temperature. Such treatment results in high activity for the dehydration of methanol to dimethyl ether (16). The reason for the low activity of the catalyst based on RhCl(CO)-(PPh₃)₂ for ether formation is not clear.

The use of a molecular sieve zeolite as a support is of particular interest because of the influence which these materials have had in the design of conventional heterogeneous catalysts.

An active carbonylation catalyst has recently been prepared by the impregnation of a sodium-X zeolite with rhodium trichloride solution (17). As with all the other catalysts the presence of iodine is necessary. Selectivity for acetate production approached 90 per cent, the main side product being dimethyl ether. On decreasing the rhodium content of the catalyst from 1 weight per cent to 0.05 weight per cent there resulted a steady increase in the rate of reaction per unit weight of rhodium, by a factor of about 20 at 250°C, but selectivity for acetate formation declined a little. This contrasts with the situation found for rhodium nitrate on carbon where maximum effective use of the rhodium was obtained at a rhodium level of about 2 weight per cent (13). Catalysts hav-

ing lower or higher rhodium contents than this displayed a smaller rate per unit weight of metal.

Like alumina, zeolites are expected to exhibit a tendency to produce dimethyl ether from the elimination reactions of methanol or methyl iodide (18), but unlike those based on the former oxide, the zeolite carbonylation catalysts had reasonably high selectivities. Again, the reason may lie in the treatment of the support before use. The zeolite was apparently not subjected to high temperature drying and, in any event, impregnation with the rhodium salt took place in aqueous solution.

These observations naturally lead one to suspect that support pretreatment procedure may have a very great influence on the catalytic behaviour of the heterogenised systems, particularly when the carriers are potentially active materials such as alumina, zeolites and silica.

Relative Activities of Heterogenised Catalysts

A comparison of the activities of various heterogenised catalysts for methanol carbonylation, given in the Table, reveals that the rate per unit weight of rhodium is not

markedly dependent upon the choice of support or rhodium compound used. Similar conclusions have been drawn before (11, 13). We have however seen that the selectivity for acetate production is greatly influenced by the nature of the starting materials. Furthermore, there appear to be differences in the stability of the supported catalysts. Although studies of the deactivation characteristics of these materials have not been extensive, the loss of activity with use seems to be especially noticeable with the polymer based systems. However, the use of these materials as catalyst supports is still a very recent development and significant improvements may well result from further work.

Insufficient data are available at present to enable the calculation of activities on a rate per unit active site basis (turnover number). This is due to the difficulty, typically associated with heterogeneous catalysts, of knowing just how many active centres are present in a given quantity of material under working conditions. However, if the heterogeneous forms are compared with the homogeneous catalyst (8) it can be seen in the Table that in order for the turnover numbers for the two catalyst types to be equal, it would be necessary to assume that only about 1 per cent of the total number of rhodium atoms in the heterogenised material is active. Such a figure does not appear unreasonable.

Until active site concentrations are established for these supported catalysts a more rigorous comparison of activities is not possible. Nevertheless the outstanding similarity between homogeneous and heterogeneous analogues for methanol carbonylation has been demonstrated. This state of affairs is very encouraging for we are now one step nearer in achieving the often mentioned goal of basing future catalyst design on molecular or enzymic catalysis (19). In view of the very many examples of homogeneous catalysis by complexes of the noble metals, it is most likely that a considerable number of heterogenised systems will be based on the same materials.

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