[*The science and art of catalysis has become an important factor in almost all facets of human life and civilisation itself. Catalysis in homogeneous systems has the advantage of a high reproducibility compared to heterogeneous catalysis. Transition metal complexes used as homogeneous catalysts can be tailored to have a high selectivity by a judicious selection of ligands and it is possible now to add to these systems one of the greatest advantages of heterogeneous catalysis, namely, the easy recovery of the catalyst from the reacting system. This is achieved by heterogenising the homogeneous catalyst by anchoring it to a suitable solid support. This article by Drs Rajagopal and Kuriacose reviews some of the more successful applications of catalysis by transition metal complexes, highlighting their import and the light they have thrown on the mechanism of catalysis.—Ed.*]

CATALYSIS BY TRANSITION METAL COMPLEXES: ACHIEVEMENTS AND PROMISES

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INTRODUCTION

HOMOGENEOUS catalysis by transition metal complexes has attracted great interest over the past few decades because of its practical importance in synthetic chemistry both in the laboratory and industry[1-4]. The major limitation of homogeneous catalysts, *viz.*, the difficulty in the separation of the catalyst from the products has been eliminated by the development of solid-supported transition metal complex catalysts.

Homogeneous catalysts have been used in about 20 important industrial processes[5] including the hydrogenation of olefins, hydroformylation of olefins to aldehydes, carbonylations of alcohols to acids, oxidation of olefins to aldehydes, ketones and vinyl esters and many polymerization reactions. Co-ordination catalysis has also opened a very attractive means to synthesize optically active compounds by asymmetric hydrogenation[6].

The three areas of catalysis, *viz.*, supported transition metal catalysts, metal clusters as catalysts and water-gas shift reactions which are attracting increased attention are reviewed here.

SUPPORTED HOMOGENEOUS TRANSITION METAL CATALYSTS

Over the past several years there has been growing interest in the heterogenization of homogeneous transition metal catalysts[7-11], in order to couple the advantages of both homogeneous (efficiency, reproducibility, specificity and controllability) and heterogeneous (good thermal stability, no solvent restriction and ease of separation from the reaction products) catalysts. The most widely used support has been polystyrene cross-linked with divinylbenzene containing phosphino or amino substituents for covalent bonding to the metal. Inorganic supports such as silica, molecular sieves and alumina are also used as supports for neutral homogeneous catalysts and sulfonated or aminated ion-exchange resins for ionic catalysts,

Almost all classical homogeneous catalysts, e.g., $RhCl(PPh_3)_3$, $RhH(CO)(PPh_3)_3$, $RuCl_3(CO)_2(PPh_3)_2$, $IrCl(CO)(PPh_3)_3$ have been anchored and found to catalyse a wide range of reactions including hydrogenation, hydrosilylation, hydroformylation, carbonylation, dimerization, oligomerization and polymerization.

Supported catalysts are generally less active than their purely homogeneous counterparts because of the presence of inaccessible sites in the former. However, a number of catalysts have been found to be more active after their immobilization[12-15]. Parameters like type of support material, cross-link densities, solvent polarity and size of substrates influence the activity and selectivity. The polymer matrix offers advantages besides simple immobilization. For example with resin bound $RhCl(PPh_3)_3$ catalysts by controlling the degree of resin swelling, the diffusion of large and small olefins into the resin could be made selective so that small olefins could be hydrogenated faster than large ones. Greater positional selectivity has also been achieved in the reduction of non-equivalent olefinic sites within the same molecule.

A large number of reviews[7-11] have covered this subject till 1978. Since 1978 Pittman and his group[16-21] have investigated the versatile homogeneous hydroformylation catalyst $RhH(CO)(PPh_3)_3$ supported on poly (styrene-divinylbenzene) resins and obtained remarkably high normal/branched aldehyde selectivities. Polymer-bound $Ru(CO)_3(PPh_3)_3$ has been used as a hydroformylation catalyst without any noticeable isomerization.

A Rh(I) complex, using the bidentate ligand, anthranilic acid anchored to polystyrene beads has been prepared by Holy[23]. This highly selective stable catalyst has been used for the hydrogenation of a variety of olefinic and aromatic hydrocarbons, carbonyl, nitrile and nitro functional groups for hundreds of runs without substantial loss of activity. Another Rh(I) complex prepared with 20% divinylbenzene-polystyrene copolymer supported η^5-cyclopentadienyl ligand has been reported[24] to be effective in hydrogenation of olefins, aldehydes, ketones, isomerization and disproportionation of olefins and hydroformylation.

Phosphinated polystyrene supported $PdCl_2Py_2$[25] and $Pd(OAc)_2$[26] have been used for the hydrogenation of soyabean oil and oligomerization of 1,3-butadiene respectively. Vapour phase catalytic hydrogenation and isomerization of olefins have been attempted using Rh(I) complex bonded to phosphine group on polystyrene-coated silica gel[27]. A satisfactory supported version of the versatile $RuCl_2(PPh_3)_3$ has been prepared very recently and used as an isomerization catalyst[28].

Polymer supported catalysts are also used for stereoselective[29] and asymmetric hydrogenation[30-31] of olefinic substrates. The use of polymer supported catalysts has been extended to inorganic substrates[32]. For example, a Cu(II) complex supported on cross-linked poly (4-vinyl pyridine) has been used as catalyst for the oxidation of thio salts to sulphates by molecular oxygen at ambient temperatures.

The more promising transition metal cluster catalysts have also been immobilised on a support like phosphinated poly (styrenedivinylbenzene)[33]. While the rates are lower with the supported catalysts, the influence of the various parameters is the same as with homogeneous catalysts[34].

METAL CLUSTERS AND HYDROGENATION OF CO

Since the classical Fischer-Tropsch process is generally unattractive owing to the economic constraints imposed by costly separation and purification processes, much attention has been focussed on the homogeneous metal cluster catalysed Fischer-Tropsch synthesis. The key factor is the selectivity and homogeneous metal cluster catalyst systems are considered to be very promising. If a molecule such as CO were bound to a metal cluster so that the carbon and the oxygen form bonds with two different metal atoms in the cluster, the

net effect would be to increase the O–O bond distance, which in turn makes the carbon monoxide much more susceptible to reduction by a second reactant such as H_2[35-39]. The clusters can be solubilized and hence possess the experimental advantages of the mononuclear homogeneous catalysts. Several adjacent metal atoms in a cluster will act something like the surface of a bulk metal and at the same time will retain the advantages of homogeneous catalysts in providing selectivity and demanding mild operating conditions.

The idea of dual coordination of CO on metal clusters has led to the use of the following clusters, viz., $Ru_3(CO)_{12}$[40], $Os_3(CO)_{12}$[40-41], $Ir_4(CO)_{12}$[40-41] and $Rh_6(CO)_{16}$[42] as catalysts for the hydrogenation of carbon monoxide to hydrocarbons. $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ in toluene have been found to catalyse the reduction of carbon monoxide to methane under mild conditions ($140°C$ and 1-3 atm.) but the rate is very slow, giving 1% conversion in 3-5 days[41]. A large number of mononuclear catalysts have been found to be inactive which lends further support to the idea that more than one metal centre is necessary for the catalytic formation of hydrocarbons from synthesis gas.

Muetterties *et al.*[43] have used molten $NaCl \cdot 2AlCl_3$ as solvent instead of toluene, keeping in mind that the carbonyl oxygen–aluminium interaction (M–C–O–Al) can favour the hydrogenation reaction. Among a large number of mononuclear and cluster carbonyls tested in the above solvent $Ir_4(CO)_{12}$ has been found to be most efficient, the primary product being ethane. Masters and Van-Doorn[40] have employed Ru, Os and Ir cluster carbonyls for the hydrogenation of CO under stringent conditions ($300°C$, 100 atm.) to yield hydrocarbons upto C_{30}, but during the reaction the metal clusters had broken down into mononuclear species. In order to prevent cluster rupture, they have used a 'capped complex' $Ru_3(CO)_9[(PBu_3)_3SiCH_3]$ prepared from $Ru_3(CO)_{12}$ and a 'cap' liquid, viz., methyltris (di-*n*-butyl-phosphine) silane for the hydro-

genation of CO to methane, ethane, propane and butane at $300°C$ and 150 bar[44].

There are several patents on soluble rhodium complex catalysis[42,45a-b] for the hydrogenation of carbon monoxide under high pressure (*ca.* $3,000$ atm. CO/H_2) to give ethylene glycol as the major product (*ca.* 70%). A possible catalyst precursor $Rh(CO)_2(acac)$ has been used in the above reactions and it is believed that anionic rhodium clusters of the kind $[Rh_6(CO)_{30}]^{2-}$ are responsible for the catalysis[45f].

In addition to homonuclear rhodium complexes, several heteronuclear metal clusters of the type $[M_xM'_{12-x}(CO)_{30}]^{2-}$, where M and M are different metals selected from among Co, Rh, Ir ($x = 1$ to 11) have been used as catalysts in the reaction between CO and H_2 to produce oxygenated products[45d,g]. Continued research on the rhodium system has given improved results at lower pressures[45a]. It is expected that this process based on rhodium complexes will go into commercial operation in the near future.

It has been stated that no mononuclear complex has been shown to function as catalyst for the hydrogenation of the very strong triple bonds in dinitrogen or carbon monoxide. However, Rathke and Feder[46] observed the $HCO(CO)_4$ catalysed hydrogenation of CO in *p*-dioxane at 300 atm./$182°C$. Recently a number of homogeneous catalysts have been reported to hydrogenate CO to ethylene glycol and/or methanol at pressures substantially above 1000 atm.[47-50].

Bradley[49] synthesised methanol and methyl formate from carbon monoxide using $Ru(acac)_3$ at $1,300$ atm./$268°C$ where the active catalyst was found to be $Ru(CO)_5$. Keim *et al.*[48] have employed group VIII metal complexes for the synthesis of oxygenated compounds from CO. A toluene/$Co_2(CO)_8$ system has been found to be highly selective to yield methyl formate, MeOH and ethylene glycol, and a mechanism involving cobalt–formyl complexes as intermediates has been proposed.

In another study, $Ru_3(CO)_{12}$ has been used as a precursor for synthesis of methanol from CO at much lower pressures, i.e., 340 atm. Carboxylic acids as additive promote the ethylene glycol formation[51]. King et al.[52] have evaluated the various cobalt carbonyl systems as precursors for CO hydrogenation to methanol, ethanol, n-propanol and their formates at 200°C/200 atm. and concluded that the active catalytic species is $HCo(CO)_4$ and that clusters of Co are of no value in CO hydrogenation. Hydrogenation of CO using $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ in 2-methoxy ethanol also yields C_1–C_3 oxygenated compounds[32].

Though the mechanism of the homogeneous Fischer–Tropsch synthesis has been discussed in recent reviews[54,55], no consensus has emerged for the mechanism of formation of alcohols. Fahey[56] has suggested a unified mechanism in an attempt to explain the entire spectrum of products. A basic and controversial component of this scheme is the participation of formaldehyde as the key intermediate for all the products.

WATER–GAS SHIFT REACTION (WGSR)

The water-gas shift-reaction[54,57] (eqn. 1) finds industrial application in CO removal, H_2 production and the adjustment of H_2 : CO ratios in synthesis gas used

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$
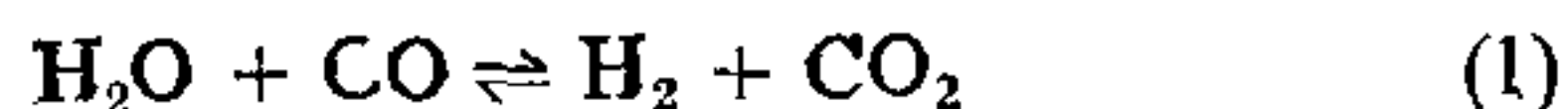
for methanation, methanol synthesis and other CO reduction processes. On an industrial scale, the shift reaction is carried out with heterogeneous catalysts at temperatures above 200°C[58]. However, the shift equilibrium is favoured by low temperatures[59]. Hence development of more active catalyst systems is presently an area of considerable interest.

Reindl and his group[60] in 1953 were the first to report the occurrence of the shift reaction in a homogeneous system in the presence of iron pentacarbonyl. Pettit et al.[61] have recently re-examined this work and shown that by careful control of pH of the reaction

mixture, CO and H_2O can be converted to formic acid or to hydrohydroxymethylated-ethylene. Laine et al.[62-66] have found that mixed ruthenium/iron carbonyls are more reactive in basic solutions than either of the metal carbonyls. Eisenberg and coworkers[59] have reported that a catalyst derived from $[Rh(CO)_2Cl]_2$, HCl and NaI in glacial acetic acid is an active homogeneous shift catalyst (250-400 Torr of CO at 80-90°C). A more detailed study has indicated that rhodium carbonyl iodide species are responsible for the catalysis[67]. A catalyst system based on platinum chloride–tin chloride chemistry has also been described for WGSR[68]. Other catalysts which have been found to be active for WGSR are (1) $Fe(CO)_5$[69,70], (2) $PtPL_3$[71,72] (L = i-Pr, Et or Ph) and (3) 2,6-bis (diphenyl-phosphinomethyl)-pyridine complexes of nickel[73].

Homogeneous catalysis of the WGSR has rekindled the interest in the use of CO + H_2O to replace H_2 in reactions such as hydroformylation and hydrohydroxymethylation and in the reduction of a variety of substrates. Hydroformylation[63,74], hydrohydroxymethylation[63,74] of olefins and hydrogenation of olefins[75], aldehydes[22], $α,β$-unsaturated carbonyls and nitriles[76,77] and nitro compounds[78,79] have been so far reported. The most noteworthy example[63] is the $Ru_3(CO)_{12}$ catalysed hydroformylation of 1-pentene by H_2O and CO yielding 98% n-hexanal and 2% 2-methylpentanal which is one of the highest selectivities for straight chain aldehydes.

Based on the literature available on homogeneous WGSR, this simple reaction appears to offer great promise in synthetic chemistry.

CONCLUSION

It is clear that the results obtained with supported transition metal complex catalysts open up new horizons for the exploitation of chemical reactions. It is possible to prepare supported transition metal complex catalysts with high activities and selectivities giving rise to a new class of catalysts which while

combining the advantages of both homogeneous and heterogeneous catalysts are superior to both.

Metal cluster catalysis is in the experimental stage and the mechanistic aspects are not fully understood. However, a large number of metal clusters which are yet to be examined as catalysts have been prepared and one is likely, as in other cases of catalysts, to arrive at practically advantageous systems in this area even before fully understanding their behaviour. The possibility of the use of carbon monoxide and water mixture for hydrogenation and hydrohydroxymethylation provides new ways of using a mixture of CO and H_2 in organic synthetic reactions.

Homogeneous catalysis by metal complex catalysts promises to provide novel and less laborious means of synthesising many useful compounds, to lead to new procedures and process for exploiting chemical reatcions and to hasoen our basic understanding of catalysts and catalysis.

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