

# Combined Homogeneous and Heterogeneous Catalysts

## SYNERGISTIC NON-LEACHING TETHERED SYSTEMS

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A number of both large- and small-scale homogeneous catalytic processes have been in commercial operation for many years (1–3), and a significant proportion of these depend on platinum group metals catalysts, sometimes involving more than one metal. The *Cativa* process operated by BP Chemicals for the production of acetic acid from methanol, has recently been using a soluble iridium/ruthenium catalyst system which includes both of these features (4).

In general, homogeneous processes are characterised by both high chemical and high energy utilisation efficiencies but a major deterrent in the further exploitation of this methodology has been the perceived inability to readily separate the products from the catalysts. Attempts to overcome this difficulty have included ligand modification, biphasic catalysis and efforts to support homogeneous catalysts on polymeric and inorganic supports. The use of supports for the catalysts has in the past been only partially successful as most of these systems have lost catalytic metal species into solution during the reactions.

The recent results reported by R. J. Angelici and H. Gao of the Iowa State University, U.S.A., are therefore of particular interest, because they result from combining the attributes of a firmly tethered homogeneous catalyst with synergistic assistance from a silica-supported metal-particle heterogeneous catalyst (5–7). These effects were demonstrated in arene hydrogenation, and such a combination catalyst has been called a “tethered complex on a supported metal”, TCSM.

In the earliest of these three papers (5), the first examples of TCSM catalysts were reported. Activity for the hydrogenation of toluene to methylcyclohexane was substantially higher than

that of the tethered complex or of the supported metal separately (40°C and 1 atm hydrogen). Rates and turnover frequencies, TOF, were low but the results indicated that there was potential for more combination reactions of this type. Two TCSM catalysts were prepared by tethering one of the rhodium isocyanide complexes,  $\text{RhCl}(\text{CO})[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_2$  (Rh-CNR<sub>3</sub>) or  $\text{RhCl}[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]$  (Rh-CNR<sub>1</sub>), to a silica supported palladium metal catalyst (Pd/SiO<sub>2</sub>) by refluxing in toluene for 4 hours, see Figure 1.

### Hydrogenation of Arenes

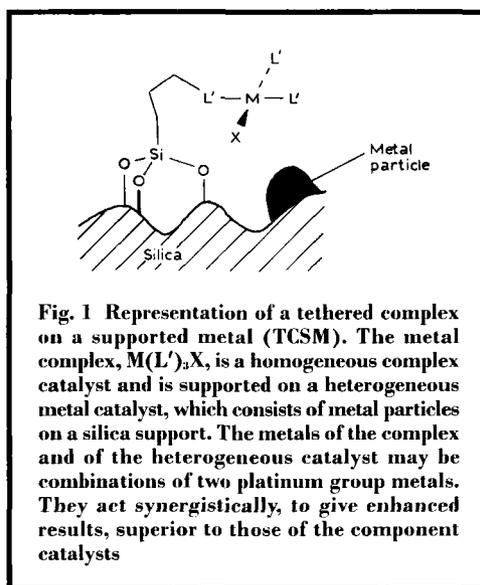
In a more recent paper (6) on this topic, rhodium and platinum isocyanide complexes  $\text{RhCl}(\text{CO})[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_2$  (Rh-CNR<sub>3</sub>),  $\text{RhCl}[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]$  (Rh-CNR<sub>1</sub>), and  $\text{PtCl}_2[\text{CN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3]_2$  (Pt-CNR<sub>3</sub>) were tethered to the SiO<sub>2</sub>-supported platinum group metal heterogeneous catalysts M-SiO<sub>2</sub> (M = Pd, Pt, Ru) to give the TCSM catalysts: Rh-CNR<sub>3</sub>/Pd-SiO<sub>2</sub>, Rh-CNR<sub>1</sub>/M-SiO<sub>2</sub> (M = Pd, Pt, Ru) and Pt-CNR<sub>3</sub>/Pd-SiO<sub>2</sub>, respectively. These TCSM systems were used to catalyse the hydrogenation of arenes (Rh-CNR<sub>3</sub>/Pd-SiO<sub>2</sub> and Rh-CNR<sub>1</sub>/M-SiO<sub>2</sub>) and cyclohexanone (Pt-CNR<sub>3</sub>/Pd-SiO<sub>2</sub>) under the same mild conditions of 40°C and 1 atm hydrogen. They again showed activities that are higher than those of the homogeneous Rh (or Pt) isocyanide complex by themselves, the SiO<sub>2</sub>-supported metal heterogeneous catalyst itself, or the Rh (or Pt) complex catalyst tethered to SiO<sub>2</sub> itself. The activities of the TCSM catalysts were strongly affected by the nature and loading of the supported metal in the catalyst. Of the three SiO<sub>2</sub>-supported metal catalysts, M-SiO<sub>2</sub> (M = Pd, Pt, Ru), the Rh complex Rh-CNR<sub>1</sub> tethered on Pd-SiO<sub>2</sub> gave the

highest activity for the hydrogenation of toluene (TOF = 5.5 mol H<sub>2</sub> (mol Rh min)<sup>-1</sup> and turnover number, TON = 2420 mol H<sub>2</sub> (mol Rh)<sup>-1</sup> during 8.5 h). The Rh-CNR<sub>2</sub>/Pd-SiO<sub>2</sub> catalyst with 10 wt.% Pd is more active than its counterparts with higher or lower Pd loadings. Spectral studies using diffuse reflectance infrared Fourier transform (DRIFT) measurements on the TCSM catalysts before and after use for toluene hydrogenation showed that the isocyanide ligands remained co-ordinated to the Rh (or Pt) centre, even after extended use. Furthermore, atomic emission spectroscopic analysis of the hydrogenation solutions indicated that there was no leaching of Rh (or Pt) into the solutions.

One possible mechanism of these reactions, which may help to explain the high activities of the TCSM catalysts, involves considering the supported palladium particles as the sites at which hydrogen is dissociated and spills over onto the silica. The tethered homogeneous complex may bind and activate the arene substrate, and this then reacts with the spillover hydrogen, thus producing the synergistic effect.

### Hydroformylation of 1-Octene

In another paper from the same laboratory, the hydroformylation of 1-octene was studied under atmospheric pressure using rhodium carbonyl thiolate complexes tethered to silica (7). It was shown that these catalysts are highly active for 1-octene hydroformylation in the presence of phosphine donor ligands at 60°C and 1 atm. The high activity resulted from the stabilisation of Rh(SR)(CO)<sub>2</sub>PR' (I) species on the catalyst surfaces. High selectivity to aldehyde was produced and the *n*:*iso* product ratios could be widely varied by choosing an appropriate phosphine (R' in (I)). The catalysts were easily separated from the reaction mixtures and the catalyst activity could be maintained through at least three cycles over a total period of 69 hours, during which time there were 1273 (mol aldehyde (mol Rh)<sup>-1</sup>) turnovers. The hydroformylation rate, conversion, and chemo- and regioselectivity were markedly affected by the phosphine donor and the PR':Rh mole ratio. With the P(OPh)<sub>3</sub> phosphine ligand, a partic-



**Fig. 1** Representation of a tethered complex on a supported metal (TCSM). The metal complex,  $M(L')_3X$ , is a homogeneous complex catalyst and is supported on a heterogeneous metal catalyst, which consists of metal particles on a silica support. The metals of the complex and of the heterogeneous catalyst may be combinations of two platinum group metals. They act synergistically, to give enhanced results, superior to those of the component catalysts

ularly fast reaction time and high TOF of 1.19 min<sup>-1</sup> was achieved, together with a high *n*:*iso* ratio of 12.0.

It can be anticipated that further investigations on the effective tethering of organometallic catalysts to inorganic supports which carry catalytic metal particles will lead to more examples of synergistic effects in TCSM catalysts. This could result in the emergence of a broad range of possible applications in both the speciality and large scale chemical processing areas.

### References

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