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A new technique for anchoring homogeneous catalysts

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Heteropoly acids have been found to serve as anchoring agents between a support material and the metal atom of a homogeneous catalytic complex.

Interest in the ability to attach active homogeneous catalysts to an insoluble support material has been on-going for over twentyfive years.[1–5] To date, virtually every example of such supported homogeneous catalysts has involved some method for placing a ligand in or on a solid material and then using this 'heterogenized' ligand to prepare a catalytic complex. With this form of attachment, the metal atom could be removed by a ligand exchange reaction possibly with some of the product, substrate molecules or other species present in the reaction mixture. In most cases the activity and selectivity of these heterogenized complexes were lower than those observed with the corresponding homogeneous species and on attempted re-use the activity and selectivity of these heterogenized complexes were frequently lost. This approach, which requires the incorporation of the ligand onto a solid material, is particularly difficult to apply with most of the chiral ligands used in the highly efficient enantioselective homogeneous catalysts in use today.

We describe here a procedure by which a preformed homogeneous complex can be anchored to a variety of support materials, with the resulting catalyst being at least as active as the homogeneous species and capable of being re-used many times with no loss of activity or selectivity and no evidence of catalyst leaching.[6]

These heterogenized catalysts have been prepared by using a heteropoly acid such as phosphotungstic acid (PTA) as the anchoring agent to attach a complex to a support material. This is accomplished by adding a solution of the heteropoly acid (20 μmol in 2.5 ml of alcohol) with vigorous stirring to a suspension of the support material (300 mg in 10 ml of alcohol), with stirring continued for about 3 h followed by the removal of the liquid and thorough washing of the solid. This solid is then suspended in another 10 ml of degassed alcohol and a solution of the homogeneous catalyst (20 μmol in 1 ml of alcohol) is added under an inert atmosphere, with stirring, over a 30 min period. Stirring is continued for 8 to 12 h under an inert atmosphere, the liquid removed and the solid washed thoroughly until no color is observed in the wash liquid. This material can be used directly or dried for future use.

In some of our initial work with alumina supports, a slight color was sometimes imparted to the reaction mixture which, at first, was thought to indicate some leaching of the complex. However, analysis of these reaction mixtures showed that they contained not only rhodium but also tungsten and aluminum, which indicated that this loss occurred by attrition of the alumina and not by any leaching of the complex. Using EtOH in the preparation and reaction procedures successfully removed this problem.

It has been reported that Rh and Ir complexes react with a heteropoly acid to give a material in which the metal atom is attached to the heteropoly acid through the oxygen atoms on its surface.[7] Attachment of the heteropoly acid to a support such as alumina takes place by interaction of the hydroxy groups of the acid with the support.[8] The result is the attachment of the complex to the support using a heteropoly acid with bonding to the metal atom. The ^{31}P MAS NMR chemical shifts for the phosphorous atom in PTA, PTA on alumina and the Rh(DiPamp) supported on PTA–Al_2O_3 both before and after use in a hydrogenation were all identical, showing that the PTA remained intact throughout the entire preparation and reaction sequence.[9]

The data presented in Table 1 show the reaction rate and product ee for successive hydrogenations of methyl 2-acetamidoacrylate (**1**) run over a Rh(DiPamp) complex supported on PTA treated Montmorillonite K as well as the corresponding data obtained using the homogeneous catalyst. The first use of the heterogeneous catalyst was slower than that observed with the homogeneous catalyst and the product ee was also lower. However, when the first product mixture was removed from the reactor and a fresh solution of the starting material added to the heterogeneous, anchored catalyst, subsequent re-use proceeded significantly faster than the homogeneously catalyzed reaction with higher product ees observed as well. This catalyst was re-used fifteen times with no loss of activity or selectivity. Analysis of the product mixtures showed that if any rhodium was present it was there in an amount below the detection limit, which corresponded to less than 1 ppm. While we are not certain of the reason for the increase in activity after the first use of the heterogeneous catalyst, the fact that in some reactions the catalyst changed from yellow to a light gray–violet on use and back to yellow on exposure to air suggests that this activation may be the result of some partial reduction of the tungsten in the PTA.

One of the advantages of this approach to anchoring homogeneous catalysts is its apparent generality, in that this procedure can be used to anchor a variety of pre-formed active homogeneous catalysts onto a number of different supports. In Table 2 are listed the reaction rate and product ee data observed for the hydrogenation of **1** over several Rh complexes anchored to alumina along with the corresponding homogeneous catalyst data, while in Table 3 are given the data for the hydrogenation of **1** using Rh(DiPamp) anchored on different supports. We have also used these anchored homogeneous catalysts for the hydrogenation of a number of other prochiral substrates such as methyl 2-acetamidocinnamate, 2-actamidocinnamic acid, dimethyl itaconate and 2-methylhex-2-enoic acid. A Ru(BINAP)

Table 1 Reaction rate and product ee data from the multiple hydrogenations of **1** over a Rh(DiPamp)–PTA–Montmorillonite catalyst[a]

Use number	Rate[b]	Product ee (%)
Homogeneous	0.25	76
1	0.18	67
2	1.20	92
3	1.26	94
6	1.49	96
9	1.29	97
15	[c]	97

[a] Hydrogenation run at 25 °C under 1 atm H_2 using 20 μmol of supported Rh(DiPamp) to saturate 0.8 mmol of **1** for each run. [b] In mol of H_2 per mol Rh per min. [c] Rate data for this run were lost due to a computer malfunction.

Table 2 Reaction rate and product ee data from the multiple hydrogenations of **1** over Rh(Ligand)–PTA–alumina catalysts along with the data from the homogeneously catalyzed hydrogenations[a]

		Anchored		Homogeneous	
Ligand	Use number	Rate[b]	Ee (%)	Rate[b]	Ee (%)
DiPamp	1	0.32	90	0.25	76
	3	1.67	93		
Prophos	1	2.0	68	0.26	66
	3	2.6	63		
Me-Duphos	1	1.8	83	3.3	96
	3	4.4	95		
BPPM	1	3.75	21	7.4	84
	3	8.15	87		

[a] Hydrogenation run at 25 °C under 1 atm H_2 using 20 μmol of supported Rh(ligand) to saturate 0.8 mmol of **1** for each run. [b] In mol of H_2 per mol Rh per min.

Table 3 Reaction rate and product ee data from the multiple hydrogenations of **1** over a Rh(DiPamp) catalyst on different PTA modified supports[a]

Support	Use number	Rate[b]	Ee (%)
Montmorillonite K	1	0.18	67
	3	1.26	94
Carbon	1	0.07	83
	3	0.41	90
Alumina	1	0.32	90
	3	1.67	93
Lanthana	1	0.38	91
	3	0.44	92

[a] Hydrogenation run at 25 °C under 1 atm H_2 using 20 μmol of supported Rh(ligand) to saturate 0.8 mmol of **1** for each run. [b] In mol of H_2 per mol Rh per min.

complex anchored to PTA treated alumina was used for successive hydrogenations of **1** and dimethyl itaconate with the reaction rate and product ee increasing after the first use in both cases. Analysis of the product mixtures from these reactions found no detectable ruthenium present.

In every instance, the reaction rates and product ee were at least equal to and frequently better than the results obtained using the corresponding homogeneous catalyst, especially when the catalysts were re-used. In some instances, even the first use of the catalyst gave superior results. Heteropoly acids other than PTA were also successful anchoring agents.

This anchoring procedure has also been applied to achiral complexes with similar results. For instance, hydrogenation of hex-1-ene over a Wilkinson's catalyst anchored to PTA treated alumina proceeded 2–3 times faster than the corresponding homogeneously catalyzed reaction, even on the first use of the heterogenized material. A Rh(dppb) complex anchored to a PTA modified alumina was used for several successive hydrogenations of hex-1-ene with a combined substrate : catalyst ratio of about 8000 : 1. An analysis of the product mixtures from these reactions found no detectable rhodium present.

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Notes and references

1 J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti and D. N. Marquardt, *J. Am. Chem. Soc.*, 1972, **94**, 1789.
2 W. Dumont, J.-C. Poulin, T. P. Daud and H. B. Kagan, *J. Am. Chem. Soc.*, 1973, **95**, 8295.
3 L. L. Murrell, *Advanced Materials in Catalysis*, Academic Press, New York, 1977, ch. 8.
4 V. Isaeva, A. Derouault and J. Barrault, *Bull. Soc. Chim. Fr.*, 1996, **133**, 351.
5 U. Nagel and J. Leipold, *Chem. Ber.*, 1996, **129**, 815.
6 S. K. Tanielyan and R. L. Augustine, *U.S. Pat. Appl.*, 08/994,025; *PCT Int. Appl.*, WO-9828074; *Chem. Abstr.*, 1998, **129**, 109217.
7 M. Pohl, D. K. Lyon, N. Mizuno, K. Nomiya and R. G. Finke, *Inorg. Chem.*, 1995, **34**, 1413.
8 Y. Izumi, R. Hasere and K. Urabi, *J. Catal.*, 1983, **84**, 402.
9 The MAS NMR spectra were obtained by Xiaolin Yang, Engelhard Corp., Iselin, NJ, USA.

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