Remarkable activity, selectivity and stability of polymer-supported Pt catalysts in room temperature, solvent-less, alkene hydrosilylations

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A polystyrene-resin supported Pt catalyst displays higher conversion, remarkably improved selectivity and excellent recyclability relative to Speier's catalyst in the room temperature solvent-less hydrosilylation of oct-1-ene using trichlorosilane.

Alkene hydrosilylation is an important reaction both on a laboratory and an industrial scale. Though many metal complexes have been reported as useful catalysts,[1] since the discovery by Speier *et al.* in 1957 that hexachloroplatinic acid is a potent catalyst even under ambient conditions,[2] Pt complexes have become the catalysts of choice. The remarkable turnover frequencies displayed by Pt-based species, and the fact that they can be used not only with alkyl and alkoxysilanes but also with chlorosilanes, explain their dominance in industrial processes. Paradoxically, however, these high activities coupled with the exothermicity of alk-l-ene hydrosilylation can lead to a rapid temperature rise in reactions, and the occurrence of a significant level of alkene isomerisation. The so-formed internal alkenes react much more slowly, and in any event limit the conversion of alk-l-enes to useful terminally silylated products.

There has been significant earlier work on the immobilisation of Pt-based catalysts using both inorganic and polymer supports, aimed at producing experimentally and technologically convenient analogues of soluble catalysts.[3,4] Likewise Rh-based species,[5] and recently Mn-based catalysts,[6] have been examined in this context. While these reports have demonstrated active heterogeneous catalysts, data on the activity and selectivity with prolonged use are rare, particularly with the more difficult chlorosilane reactants, and equally importantly meticulous evaluation of the contribution from leached soluble catalyst has generally been absent. We now make a preliminary report on our studies of in-house prepared polystyrene and polymethacrylate resin-supported Pt catalysts in the hydrosilylation of oct-l-ene using trichlorosilane in the absence of any solvent, and at ambient temperature.

Precursor resins (PR1–PR5) were prepared by suspension polymerisation[7] using the comonomer mixtures shown in Table 1. The functional group content [–CH2Cl from vinylbenzyl chloride (VBC) or epoxide from glycidyl methacrylate (GMA)]

and surface area of the resultant resins are also shown in Table 1. PR1–PR5 were aminated by treatment with excess trimethyl-ethylene diamine/NaH in THF at 60 °C for 48 h to yield AFRI–AFR5 (Table 2), and finally each of these was loaded with Pt by treatment with an excess of K_2PtCl_4 in water to yield polymer catalysts C1–C5 (Scheme 1, Table 2). The activity and selectivity of C1–C5 were assessed in the reaction of oct-l-ene (20 mmol) and trichlorosilane (10 mmol) in 8 cm³ sealed Pyrex vials in the absence of any solvent at room temperature. Polymer catalysts containing 10^{-3} mmol of Pt were employed

Table 2 Analytical data for catalyst resins

Precursor resin	Amine functionalised resin		Pt catalyst resin	
	Code	Diamine content[a]/ mmol g⁻¹	Code	Pt content[b]/ mmol g⁻¹
PR1	AFR1	2.85	C1	1.4
PR2	AFR2	1.5	C2	0.9
PR3	AFR3	1.5	C3	0.9
PR4	AFR4	0.9	C4	0.4
PR5	AFR5	1.7	C5	0.5

[a] Calculated from N% content. [b] ICPES analysis of acid digested resins.
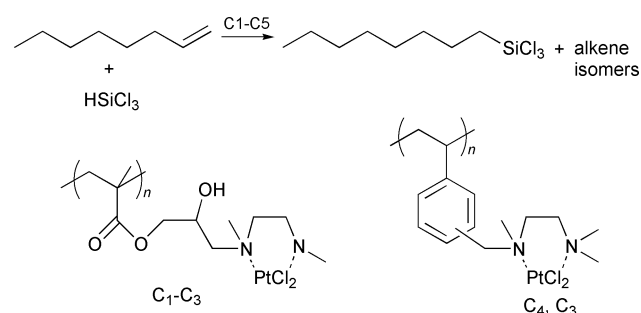
Scheme 1 Oct-1-ene hydrosilylation using trichlorosilane catalysed by polymer catalysts C1–C5.

Table 1 Composition of precursor resins

Precursor resin[a]	Comonomer mixture (vol %)[b]						Porogen (Porogen/ monomer vol ratio)	Resin properties	
	EGDMA	GMA	DVB	Est	St	VBC		Epoxide/ CH2Cl content/ mmol g⁻¹	Surface area[c]/m² g⁻¹
PR1-Me-G	2	98	—	—	—	—	None	6.9/—	~0
PR2-Me-M	50	50	—	—	—	—	Toluene (2:1)	3.5/—	113
PR3-Me-M	50	50	—	—	—	—	Octan-2-one (2:1)	3.5/—	119
PR4-St-M	—	—	53	13	0	34	Isooctane (1:1)	—/2.3	100
PR5-St-CM	—	—	10	2	53	34	2-Ethylhexanoic acid (1:1)	—/2.3	33

[a] Me = methacrylate-type; St = styrene-type; G = gel-type; M = macroporous type; CM = collapsed macroporous.[8] [b] EGDMA = ethyleneglycol dimethacrylate; GMA = glycidyl methacrylate; DVB = divinylbenzene. [c] N2 sorption, BET analysis.
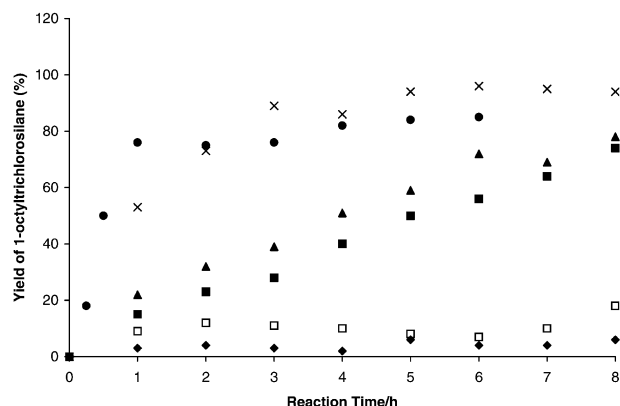
Fig. 1 Yield of 1-octyltrichlorosilane as a function of time in oct-1-ene hydrosilylations using trichlorosilane catalysed by: (●) Speier's catalyst; (◆), C1; (■), C2; (▲), C3; (×) C4; (□), C5.

Fig. 2 Yield of 1-octyltrichlorosilane from oct-l-ene and trichlorosilane catalysed by C1–C5 with the heterogeneous catalyst removed after 1 h.

and compared to the performance of soluble Speier's catalyst (5 wt% $H_2 PtCl_6 \cdot 6H_2O$ in isopropyl alcohol using 10^{-3} mmol Pt). The appearance of l-octyltrichlorosilane and octene isomers (oct-2-, -3- and -4-enes as a non-resolved group) was monitored by GC analysis using nonane as an internal standard. The mole ratio of oct-l-ene: trichlorosilane of 2 : 1 was chosen to highlight any isomerisation induced by the catalyst while minimising competition from the hydrosilylation reaction, *i.e.* isomerisation was deliberately given a competitive advantage. In addition, to demonstrate the high activity and stability of the polymer catalysts (identified in preliminary ligand screening experiments) each sample reported here was utilised in four previous reactions, *i.e.* the data here refer to the fifth cycle of use in each case. Data for Speier's catalyst refer to its first use. No attempt was made to recover and re-use this homogeneous species.

The results of the catalytic studies are summarised in Fig. 1. The behaviour of the homogeneous catalyst is as expected from the literature. The conversion of trichlorosilane to l-octyltrichlorosilane reached *ca.* 75% in *ca.* 1 h. However, simultaneously the isomerisation of oct-l-ene to internal alkenes was *ca.* 60%. (Note initial mole ratio oct-l-ene : trichlorosilane is 2 : 1.) The performance of the polymer catalysts varies considerably. Catalyst C1 shows very low activity. Since this is a polar gel-type methacrylate-based resin, it would not be expected to swell in the non-polar reaction mixture and presumably therefore catalytic Pt sites are accessed only very inefficiently as a result of poor mass transport. Likewise though catalyst C5 is a non-polar styrene-based resin, and is nominally macroporous, in fact the surface area of this species is very low (*ca.* 30 m² g⁻¹), and we believe the morphology is substantially collapsed.[8] Catalysts C2 and C3 perform well yielding *ca.* 70% l-octyltrichlorosilane after *ca.* 6 h. Though these are polar methacrylate-based resins, they have permanent macroporous morphologies with good surface area (*ca.* 110–120 m² g⁻¹). Catalyst C4 is significantly the most active yielding *ca.* 70% l-octyltrichlorosilane after 2 h, and ultimately delivering *ca.* 90%. In this respect it performs better than Speier's catalyst. C4 is a non-polar styrene-based resin and is macroporous with a good surface area (*ca.* 100 m² g⁻¹). It clearly offers no significant mass transfer limitations. Furthermore with C4 the level of oct-l-ene isomerisation is only *ca.* 9%, and indeed less than *ca.* 4% with the other polymer catalysts. C4 therefore is also significantly more selective in favour of hydrosilylation than Speier's catalyst. These results are even more remarkable when it is borne in mind that these data refer to the fifth cycle of use of this sample of C4.

Overall it is tempting to conclude that the heterogenised Pt complexes are highly selective in favour of the hydrosilylation reaction, and the low level of alkene isomerisation observed may be due to very low levels of leached Pt species acting as a less selective homogeneous catalyst.
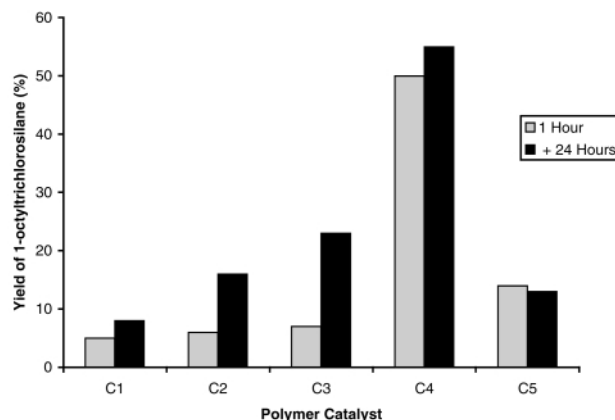
Some assessment of the level of Pt leaching with C1–C5 was obtained from a sixth cycle of use of these samples in which hydrosilylations were run as before for 1 h, and then the reaction mixtures decanted from the resin beads, and the mixtures monitored for a further 24 h. The results are shown in Fig. 2. The left-hand bar in each case shows the percentage of 1-octyltrichlorosilane formed after 1 h in the presence of polymer catalysts, and the right-hand bar the conversion after a further 24 h in the absence of polymer catalysts. Though some increase in l-octyltrichlorosilane is seen, particularly with C2 and C3 (presumably reflecting the presence of some soluble catalytic species), the effect is not large. With C4 the small additional conversion seen after 24 h is within the analytical experimental error. In addition no measurable increase in the amount of isomerised alkene is observed, which remains very low. Thus it seems that the level of Pt leached is itself very low, or any species in solution is inactive as a catalyst either in hydrosilylation or in isomerisation.

Thus we have succeeded in producing a polymer-supported Pt alkene hydrosilylation catalyst (C4) with activity comparable to that of Speier's catalyst, with greatly enhanced selectivity in terms of minimising concurrent alkene isomerisation, and with considerable long term recycling stability along with minimal Pt leaching characteristics. The catalyst performs well with trichlorosilane as the silylating agent and displays considerable potential for both small- and large-scale application. We are currently undertaking a more detailed investigation to improve our understanding of this catalyst system.

Notes and references

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