Optimisation of Polystyrene Resin-supported Pt Catalysts in Room Temperature, Solvent-less, Oct-l-ene Hydrosilylation using Methyldichlorosilane

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Abstract: Six precursor resins with systematic variation of porous parameters were prepared by suspension polymerisation using specific compositions of divinylbenzene, styrene vinylbenzyl chloride (VBC) and 2-ethylhexan-l-ol (a porogen). Surface areas from N_2 sorption and BET analysis were ~ 2-170 m^2g^{-1}. The VBC content in each case was 38 mol% and these groups were aminated using the sodium salt of trimethylethylene diamine. Pt was introduced onto each resin at three different loadings (~0.03, ~ 0.2 and ~ 0.4 mmol g^{-1}) by appropriate manipulation of K_2PtCl_6.

The matrix of 18 resin-supported Pt complexes was then assessed for catalytic activity in the room temperature, solvent-less, hydrosilylation of oct-l-ene using methyldichlorosilane such that alkene: silane: Pt ratio was fixed at $2:1:1x10^{-3}$. Though all the catalysts showed activity lower than that of homogeneous Speier's catalyst, most were sufficiently active to be potentially valuable heterogeneous catalysts in the laboratory, and indeed the plant. The most lightly loaded resins proved to be the least active. The remainder were recycled 5 times, and the best performers, the most highly loaded species, a further 5 times making 10 consecutive uses in all. A strong dependence on the porous structure of the resins was demonstrated with the activity rising systemically with the surface area. The two highest surface area highest loaded species displayed good activity even when used for the tenth time. The level of concurrent alkene isomerisation observed was very low throughout (<1%) making these heterogeneous species very selective as well as highly active. Overall the derived catalysts are excellent candidates for use in the research laboratory, and with further development could also be valuable in continuous processes.

INTRODUCTION

The use of solid supports in the rapid and automated synthesis of compounds using a split and mix combinatorial methodology or a parallel synthesis approach has centred primarily on building the target compounds attached to the solid phase. So-called solid phase organic synthesis (SPOC) has in fact expanded the concept of solid phase peptide synthesis (SPPS) [1-3]. The overwhelming problem with this methodology is the inability to monitor in a sensitive manner the molecular structural changes achieved at each stage of a multi-step synthesis, without cleaving appropriate samples from the support for analysis by solution phase NMR and mass spectrometry, etc. In this context considerable advances have been made in achieving at least some qualitative measure of the molecular structure of support-bound species using techniques such as gel-phase magic angle spinning NMR and single bead FTIR [4-6]. However, for mainstream organic synthetic chemists there remains considerable frustration in achieving adequate and convenient monitoring of solid phase reactions, and this has stimulated the idea of performing the solid phase chemistry in reverse with all reagents, catalysts, separation media, etc., as heterogeneous species and the molecule being assembled present in solution. This immediately offers the opportunity to sample the reaction solution at any stage in a multi-step reaction, and to characterise the molecular structure of the soluble component(s) using all the powerful analytical tools available in a modern synthesis laboratory. At the same time the use of insoluble reagents, catalysts etc. also allows all the advantages of robotic handling and fast combinatorial or parallel synthesis developed in SPOC. The power of this approach has been highlighted by remarkable work from Ley's laboratory where it has been shown that by appropriate design of synthetic strategies it is possible to use only solid phase reagents, catalysts and scavengers together with solvents, to achieve quite sophisticated multi-step synthesis in high yields and excellent purity [7-11]. Others have also now adopted this approach [12, 13].

This strategy is possible however only with the availability of suitable high quality supported reactive species, and indeed the range offered by chemical supply houses is now growing almost weekly. An early comprehensive review of supported reagents and catalysts was published by Sherrington and Akelah [14] in 1981 who cited 581 references. However, Ley and his team [15] have now produced a remarkable up-dated compilation with

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selective citation of 1487 references on supported reactive species and their application in particular syntheses.

A very useful transformation in organic chemistry is the hydrosilylation of alkenes and this is used widely on both an industrial and laboratory scale. A particularly active and selective homogeneous catalyst was discovered by Speier [16] and since then Pt complexes have become the catalysts of choice. Not surpisingly there have been reports on attempts to immobilise Pt complexes for use in alkene hydrosilylation, indeed the early work has been reviewed [17, 18]. The nature of the ligand seems to play an important role [19-21] in controlling activity. Michalska and her group have also carried out considerable work on polymer-supported Rh catalysts in hydrosilylations [22-26], and in the case of polyamide-based supports have shown the microporous structure of the latter to influence the ratio of branched to linear products [24]. Recently a polymer-supported Mn-based system has also been described [27] but this requires elevated temperature for significant activity.

Although these reports demonstrate active polymer-supported metal complex alkene hydrosilylation catalysts, little attempt has been made to study any potential metal leaching and its role in the observed catalysis. Likewise little attention has been paid to the level of the important side-reaction, alkene isomerisation, induced by the catalysts. Finally most of these studies have avoided the use of the experimentally difficult to handle chlorosilanes. All of these factors are important in developing a supported Pt catalyst with real potential for exploitation in combinatorial chemistry, and recently we made our first reports on systems which we feel offer considerable potential in this respect [28, 29].

We have shown that gel-type resin supports are not useful in hydrosilylation reactions because these do not swell in alkenes and silanes [28]. However, macroporous resins are much more suitable, with polystyrene-based species being better than polymethacrylate-based ones. This difference seems to arise simply because of the more hydrophobic nature of the polystyrenics [29]. The previous group of resins investigated produce very active catalysts with good long-term stability and low Pt leaching characteristics. However, the resins involved were prepared with a variety of ligand and Pt loadings as well as a breadth of morphologies. The present study was aimed at focussing more precisely on a number of key structural parameters, namely the Pt loading and specific porosity parameters such as surface area. To this end six tailored polystyrenic resins have been prepared with a fixed vinylbenzyl chloride content and systematic variation of surface area and other interrelated porosity parameters. Following amination the resins have been loaded at three different levels with Pt. The present report describes the synthesis, characterisation and evaluation of the resultant polymer-supported Pt alkene hydrosilylation catalysts.

EXPERIMENTAL MATERIALS

Styrene, divinylbenzene (DVB) (80% commercial grade, balance ethyl styrene); 2-ethylhexan-l-ol; N,N,N'-trimethylethylenediamine; (TriMEDA) sodium hydride; THF; oct-l-ene; methyldichlorosilane and hydrogen hexachloroplatinate hexahydrate were all obtained from the Aldrich Chem. Co. Vinyl benzyl chloride (VBC) (mixed m- and p- isomers) was from the Dow Chemical Co., and potassium tetrachloroplatinate was from Johnson Matthey.

Speier's catalyst was made up by dissolving hydrogen hexachloroplatinate in propan-2-ol (dried over molecular sieves) to a concentration of 5 wt%.

SYNTHESIS OF PRECURSOR RESINS (1A-F).

These were prepared by suspension polymerisation using procedures we have reported in detail elsewhere [29, 30]. Copolymerisations employed 50 g of monomers, and the various compositions used are summarised in Table 1. The yield of beads was 80-95% and the diameter range 212-710 μm. The FTIR spectra of the products exhibited a characteristic band at 1270 dm^{-1} assigned to the $-CH_2Cl$ stretch.

AMINATION OF RESINS (1A-F) TO YIELD (2A-F) (Scheme 1)

The ethylendiamine-based functionality in (**2a-f**) was introduced by reaction of (**la-f**) with the sodium salt of N,N,N'-trimethylethylenediamine generated by reaction of

Table 1 Composition of St/DVB/VBC Suspension Polymerised Resins(1a-f)[a)]

Resin	DVB[b)] (vol%)	ESt[c)] (vol%)	St (vol%)	VBC[d)] (vol%)	Porogen[e)]/ Monomer vol/vol)	Cl[f)] Content (mmol $^{-1}$)
(1a)	50	12	0	38	0.5	2.6
(1b)	50	12	0	38	1.0	2.4
(1c)	50	12	0	38	2.0	2.3
(1d)	25	7	30	38	0.5	3.0
(1e)	25	7	30	38	1.0	3.1
(1f)	25	7	30	38	2.0	2.9

a) See Experimental and ref [30] for details; b) 80% commercial grade; c) component in commercial DVB; d) mixed m- and p- isomers; e) 2-ethylhexan-l-ol; f) determined from elemental microanalytical data.

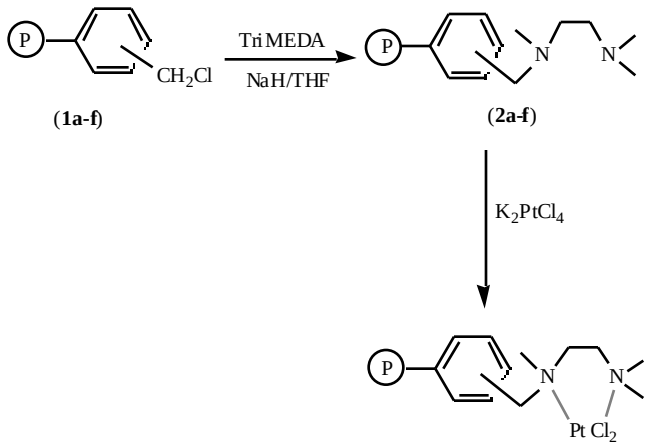
the parent amine with NaH. Full details have already been reported [29]. The data in Tables 2 and 3 indicate the %N achieved and the corresponding ligand loading.

Table 2. Elemental Microanalytical Data for Resins (1a-f), (2a-f) and (3a-f)

Resin	Carbon (%)	Hydrogen (%)	Chlorine (%)	Nitrogen (%)
(**1a**)	82.5	7.1	8.3	-
(**1b**)	82.7	7.4	9.1	-
(**1c**)	84.0	7.5	8.4	-
(**1d**)	83.4	7.2	10.4	-
(**1e**)	81.9	7.0	10.7	-
(**1f**)	82.2	7.1	10.9	-
(**2a**)	82.6	8.3	3.6	2.9
(**2b**)	76.0	7.8	3.9	2.4
(**2c**)	81.9	8.1	3.9	2.9
(**2d**)	82.5	8.3	3.4	3.8
(**2e**)	81.2	8.4	4.9	3.9
(**2f**)	83.1	8.3	2.8	3.6
(**3a**)	81.4	7.8	5.0	3.1
(**3b**)	79.6	7.8	6.5	2.8
(**3c**)	82.0	7.9	3.5	3.5
(**3d**)	81.3	8.4	3.9	3.6
(**3e**)	80.1	8.4	5.0	3.8
(**3f**)	81.4	8.3	2.7	3.6
(**4a**)	76.7	7.6	6.2	2.7
(**4b**)	74.4	7.5	8.0	2.4
(**4c**)	76.8	7.6	5.0	2.7
(**4d**)	77.1	7.8	5.2	3.5
(**4e**)	76.9	7.8	5.5	3.6
(**4f**)	78.8	7.9	3.8	3.6
(**5a**)	71.9	7.1	7.5	2.6
(**5b**)	70.0	7.0	9.6	2.2
(**5c**)	72.5	7.1	6.4	2.4
(**5d**)	72.0	7.2	6.5	3.1
(**5e**)	71.6	7.4	7.3	3.4
(**5f**)	76.2	7.7	4.2	3.4

LOADING OF PT TO YIELD CATALYSTS (3A-F), (4A-F) AND (5A-F) (Scheme 1)

The weight % Pt and ligand: Pt ratio were targeted as potentially key variables, and so the loading of Pt was controlled to produce three sets of catalysts. This is exemplified in the case of (**3a**), (**4a**) and (**5a**).



Scheme 1. Amination of chloromethylated precursor resins and loading of Pt species.

Resin (**2a**) (2 g, 2.2. mmol ligand) and K_2PtCl_4 (44.7 mg, 108 μmol) were added to a polyethylene bottle. The sample of resin was wetted with a little THF before addition of doubly distilled water (150 cm^3) to solubilise the Pt salt. The bottle was capped then shaken for 24 h at room temperature. The Pt loaded resin (**3a**) was recovered by filtration and washed with water and acetone before vacuum drying at 60°C for 18 h.

In preparing (**4a**) and (**5a**) each from (**2a**) the amount of K_2 $PtCl_4$ was increased to 224 and 447 mg respectively. In this case the Pt salt was introduced incrementally in ~ 50 mg portions to try to maintain a fairly constasnt concentration of Pt salt in the bulk solution throughout the loading procedure. The data in Table 3 show the Pt loadings achieved and the corresponding ligand: Pt ratios. Details of our Pt analysis procedure have been published [29].

CATALYSED OCT-L-ENE HYDROSILYLATIONS USING METHYLDICHLOROSILANE. (Scheme 2)

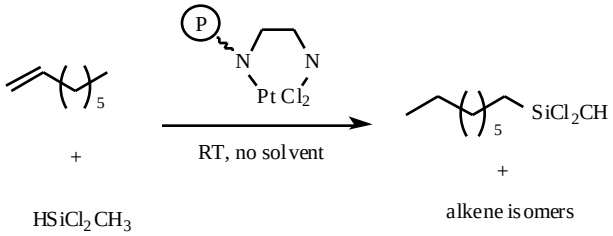
Each reaction was carried out in a sealed pyrex vial (8 cm^3) with the screw top lid fitted with a teflon-faced silicone septum. The appropriate mass of resin catalyst (containing the required amount of Pt) was weighed into the vial followed by a portion of a freshly prepared reactant mixture containing oct-l-ene (22.4 g, 0.2 mol) and methyldichlorosilane (11.5 g, 0.1 mol) together with nonane (10g) as an internal GC standard. The vial was capped and placed on a shaker at room temperature for the duration of the reaction. Each mixture was assayed at given times by using GC analysis, samples being withdrawn via the teflon-lined septum. Catalyst samples were recycled by carefully decaning off reaction supernatant mixtures and re-charging the vial with a portion of fresh reaction mixture.

Table 3. Ligand and Pt loadings of Resins (2a-f), (3a-f), (4a-f), (5a-f)

Resin	**Ligand Loading ($mmolg^{-1}$)**	**Pt Content (wt%)**	**Pt Loading ($mmolg^{-1}$)**	**Ligand/Pt Mole Ratio**	**Resin**	Ligand Loading ($mmolg^{-1}$)	Pt Content (wt%)	Pt Loading ($mmolg^{-1}$)	Ligand/Pt Mole Ratio
(**2a**)	1.1	-	-	-	(**3a**)	1.1	0.7	0.04	27
(**2b**)	0.9	-	-	-	(**3b**)	1.0	0.6	0.03	33
(**2c**)	1.0	-	-	-	(**3c**)	1.2	0.6	0.03	40
(**2d**)	1.4	-	-	-	(**3d**)	1.3	0.7	0.035	37
(**2e**)	1.4	-	-	-	(**3e**)	1.4	0.65	0.03	45
(**2f**)	1.3	-	-	-	(**3f**)	1.3	0.7	0.035	37
(**4a**)	1.0	4.1	0.21	4.5	(**5a**)	1.0	8.2	0.42	2.2
(**4b**)	0.9	3.5	0.18	4.7	(**5b**)	0.8	8.2	0.42	1.9
(**4c**)	1.0	3.7	0.19	5.0	(**5c**)	0.9	8.0	0.41	2.1
(**4d**)	1.3	4.1	0.21	5.9	(**5d**)	1.1	8.2	0.42	2.6
(**4e**)	1.3	3.7	0.19	6.8	(**5e**)	1.2	8.0	0.41	2.9
(**4f**)	1.3	3.5	0.18	7.2	(**5f**)	1.2	5.3	0.27	4.4

ANALYTICAL METHODS AND INSTRUMENTATION

Elemental microanalysis were carried out by the Microanalysis Service Laboratory at the University of Strathclyde. Inductively coupled plasma atomic absorption spectrophotometric analysis (ICP AAS) of Pt was carried out at the Centre for Particle Characterisation and Analysis, University of Paisley, Scotland. N_2/BET surface analyses were performed in-house using a Micromeritics ASAP 2000 instrument. Hg intrusion porosimetry were also performed in house using a Micromeritics Autopore II 9220. Solvent uptake measurements were carried out using a centrifugation technique reported in literature [31]. GC analyses were undertaken with a Carlo Erba Mega Series HRGC 5300 fitted with a 12 m x 0.32 mm, non-polar capilliary column (SGE BPX5) and a flame ionisation detector. FTIR spectra were collected using a Nicolet Impact 400D. 10 scans were carried out at a resolution of 4 cm^{-1} for each sample. The latter were ground and prepared as KBr discs.



Scheme 2. Catalysed hydrosilylation of oct-l-ene by methyldichlorosilane.

RESULTS AND DISCUSSION

Synthesis and Characterisation of Resins (1a-f)

Precursor resins (**1a-f**) were synthesised in good yield and good physical form. Interestingly though the vol% of VBC monomer used in each case was constant, the level incorporated into the 55 vol% DVB resins (**1a-c**) was consistently somewhat lower than that found in the 25 vol% DVB resins (**1d-f**), i.e., the level of incorporation of the VBC residues is superficially a function of the monomer feed composition. This might arise because the composition of the comonomer make-up influences the level of VBC partition between the organic (polymerising) and the aqueous phases, which in the present case seems unlikely. It might also arise if the level of hydrolysis of VBC residues (which reduces the % Cl found experimentally) which occurs is a function of the comonomer make-up, and again this seems unlikely. Finally the effect may be due to the differing reactivity of DVB and styryl carbon-carbon double bonds each with VBC, and this seems the most likely explanation. In particular the high reactivity of the first double bond in DVB isomers [32], particularly at high levels of DVB as in the case here, may serve to disfavour VBC incorporation. The expected Cl content based upon the monomer feed in Table 1 is ~ 10 wt% and this correlates well with the experimental data for resins (**1d-f**) prepared with DVB of 25 vol%. The lower values for Cl incorporation for resins (**1a-d**) prepared from 50 vol% DVB tend to confirm that DVB disfavours VBC incorporation. Overall, however, the level of functionalisation achieved meets the targeted figure and is more than adequate to form the basis of supported catalysts.

Table 4. Porosity and Solvent Imbibition Data for Resins (1a-f)

Resin	Surface Area (m^2g^{-1})		Average[a)] Pore Diameter (Å)	Total Intrusion [a)] Volume (cm^3g^{-1})	Solvent Up-take (cm^3g^{-1})		
	N_2 sorption BET	Hg intrusion			CH_3OH	Toluene	oct-l-ene
(1a)	171	172	130	0.56	0.58	0.72	0.46
(1b)	131	173	262	1.13	1.04	1.22	0.89
(1c)	22	102	1190	3.04	1.94	2.34	1.64
(1d)	76	166	130	0.54	0.49	0.80	0.43
(1e)	51	106	503	1.33	1.19	1.53	1.09
(1f)	1.5	96	606	1.45	1.01	1.40	0.81

a) From Hg intrusion data

Variation of the level of DVB and 2-ethylhexan-l-ol porogen used in synthesising resins (**1a-f**) was designed to give rise to significant changes in the morphology of the resins while keeping the degree of functionalisation roughly constant. The porosity data derived for the resins, and their corresponding response to various solvents are summarised in Table 4. Very rewardingly systematic and interrelated changes in the surface area, average pore diameter and total pore volume of the resins are apparent. The surface areas of the higher DVB-based resins (**1a-c**) are systematically larger than those of the lower DVB-based resins (**1d-f**). Within each group the surface area falls and the average pore diameters [(1a→c),(1d→f)] as the proportion of porogen used in the polymerisation rises, and likewise the total pore volume rises in parallel. All these data are consistent with the known effects of porogen on the morphology of resins produced in model DVB-styrene systems [32, 33].

The response of the resins on contact with methanol, toluene and oct-l-ene (Table 4) follow a consistent pattern, and correlates well with the dry state porosity data in the same Table. As a very general guide, use of a thermodynamically poor porogen in preparing styrenic resins causes early phase separation creating macroscopically relatively rigid and permanently porous morphologies [34]. In addition when the volume of porogen is e.g. the same as the volume of comonomers, then the total dry state pore volume generated in the resin is ~ 1 mlg^{-1}, with the latter changing systematically with the volume ratio of porogen: comonomers. This rough correlation is seen in the pore volume data in Table 4 and is also reflected in the solvent up-take data in this Table. Note that since the solvents are primarily filling pores rather than swelling the polymer gel phase itself (which is highly crosslinked in all these resins), the up-take data are very similar irrespective of the solvent. There are however, a few anomalies the most notable being the data for resin (**1f**). This has lower pore volume and solvent up-take figures than expected for the 2:1 vol/vol porogen/comonomer used in its synthesis. It seems therefore that the DVB level of 25 vol% is too low to sustain the large pore volume induced by the high porogen ratio (2:1), and the polymer matrix almost certainly shrinks permanently somewhat on drying.

In the present context however, the morphological variation in the resin supports (**1a-f**) forms the basis for a very relevant study of the effect of this parameter on the activity and selectivity of resin-supported Pt complex alkene hydrosilylation catalysts. Not the least all the resins imbibe significant levels of oct-l-ene, and this should minimise mass transport limitations involving molecules such oct-l-ene and methyldichlorosilane which do not swell polystyrene gels.

Ligand and Pt Loading to Produce Resins (2a-f) and (3, 4, 5a-f) Respectively

We have reported previously [29] our procedure (Scheme 1) for introducing trimethylethylenediamine (TriMEDA) residues onto chloromethylated polystyrene residues and the same methodology was adopted here. The ligand loadings obtained for (**2a-f**) are shown in Table 3. These correspond to ~ 50% derivatisation of the $–CH_2Cl$ groups originally present in resins (**1a-f**), and these conversions are typical of what are often seen with highly crosslinked polystyrene resins.

Using three different feed levels of K_2PtCl_6 to generate the three series of resins, (**3a-f**), (**4a-f**) and (**5a-f**), the Pt loadings and corresponding ligand: Pt mole ratios shown in Table 3 were obtained. Again it was rewarding to see that adjustment of the level of K_2PtCl_6 employed did indeed allow manipulation of the Pt content of resins over an order of magnitude (~0.04-0.4 mmol g^{-1}) with a corresponding variation in the ligand: Pt ratio. Again these are potentially important parameters in controlling alkene hydrosilylation catalyst activity and selectivity.

Hydrosilylation of Oct-l-ene using Methyldichlorosilane Catalysed by Resins (3, 4, 5a-f)

All hydrosilylations were carried out at room temperature using an oct-l-ene: silane: Pt ratio of 2:1:1 x 10^{-3}. In the case of Speier's catalyst the yield of octylmethyl dichlorosilane reached ~ 95% in 30 minutes [29] but was

accompanied by ~ 16% isomerisation of the original oct-l-ene feed (**Note** the ratio of oct-l-ene: silane was deliberately selected as 2:1 to highlight any competitive isomerisation).

The data in Table 5 show the corresponding yields of octylmethyldichlorosilane obtained after 24 h with the first use of catalysts (**3, 4, 5a-f**). Three conclusions are clear. First the activity of all the polymer-supported species is lower than that of Speier's catalyst used at the same level. However, the observed activity is good and suitable for potential use both in the laboratory and in the plant. Secondly, though the molar quantity of Pt employed was constant in all reactions, the lightly Pt loaded resins (**3a-f**) are as a group (superficially at least) of significantly lower activity than the other two groups. Thirdly, catalysts (**a-c**) derived from resins prepared with 50% DVB are more active than catalysts derived from resins prepared with 25% DVB. Clearly therefore developing catalyst systems with Pt loadings as low as 0.03 mmol g^{-1} (e.g. (**3a-f**)) seems inappropriate, although the correspondly high ligand: Pt ratio of ~30-45:1 cannot be discounted as a negative factor. Indeed future work should probe this variable carefully. The highest Pt loading employed here was ~0.4 mmol $g^{-1,}$ and again future work might examine even higher levels. Closer inspection of the data and reference to the surface area data in Table 4 also suggests that within each (**a-c**) and (**d-f)** series the activity rises with the surface area of the precursor resin used in preparing the catalysts. Very significantly, catalysts (**3e, 3f, 4e, 4f** and **5e**) all perform very poorly and this seems to be a reflection of the low surface area of these species and most likely mass transfer limitation in accessing Pt sites by both the octene and the silane reactants. The performance of (**5f**) in this context seems completely anomalous, but a clue to the apparently high activity of this species comes from analysis of the level of alkene isomerisation which occurs. For all the resin catalysts except (**5f**) the level of isomerisation detected was negligible, and so these catalysts are significantly more selective than Speier's catalyst. However the level of isomerisation was ~ 8% of the original oct-l-ene feed with (**5f**). Previously we have presented extensive experimental evidence [29] which can be best rationalised with a model in which the truly heterogenised Pt complexes have very low isomerisation activity, and that when significant isomerisation is seen with a Pt resin catalyst it arises from reaction with leached homogeneous Pt species. This indeed seems to be situation with (**5f**), and significant leaching of Pt species from this resin would explain not only the isomerisation that occurs, but also the anomalously high hydrosilylation activity displayed by this very low surface area catalyst.

Table 5 Yields of Octylmethyldichlorosilane in Run 1 of Reactions[a)] of Oct-l-ene with Methyldichlorosilane Catalysed by Resin-supported Pt (3a-f), (4a-f) and (5a-f)

Resin Catalyst	Yield (%)	Resin Catalyst	Yield (%)	Resin Catalyst	Yield (%)
(3a)	52.1	(4a)	99.8	(5a)	~ 100
(3b)	57.5	(4b)	97.8	(5b)	98.4
(3c)	50.1	(4c)	96.2	(5c)	87.4
(3d)	34.8	(4d)	48.6	(5d)	73.5
(3e)	~0	(4e)	0	(5e)	7.0
(3f)	~0	(4f)	32.6	(5f)	92.6

a) 24 h, room temperature, oct-l-ene: silane: Pt = 2:1:1 x 10^{-3}

To gain more insight into the stability of the resin catalysts and any tendency to leach Pt-based species, each of the previously used samples of resins (**4a-f**) and (**5a-f**) (i.e, the more active catalysts) were recovered and re-used a further 4 times in identical hydrosilylation reactions. On the latter occasion, i.e., the fifth use of each catalyst, the reactions were monitored with time using the GC analytical procedure. The conversion curves obtained with catalysts (**4a-f**) are shown in Figure 1 and with catalysts (**5a-f**) in Figure 2. Clearly most of those catalysts which were the highly active ones in run 1 remain very active also in run 5, i.e., (**4a-c**) and (**5a-b**). Catalysts (**4d-f**) and (**5d and 5e**) which were less active in run 1 show further loss of activity or become essentially inactive. Catalyst (**5f**) is again an interesting one because in run 5 its activity is considerably depressed and this is consistent with the earlier observation that leaching of Pt-based species was responsible for its high activity in run 1. Almost certainly successive re-use of (**5f**) leads to increasing loss of poorly bound Pt, until in run 5 little labile Pt remains. The fall in activity of the other catalysts cannot be unambiguously assigned to loss of Pt but may arise also from e.g. catalyst fouling. Catalysts (**5a**) and (**5b**) with their initially high loading of Pt and significant surface area remain particularly active in run 5 whereas the third member of this group (**5c**) shows a significant decline. This species is prepared from a precursor resin with a low surface area ~ 20 m^2g^{-1}, (Table 4) and it may be that a large proportion of active sites becomes less accessible with continued use as a result of fouling or that the more accessible and hence initially active sites lose their Pt as leached species.

To further challenge these samples of catalyst each was re-used 5 more times in identical hydrosilylation reactions with each tenth batch reaction being monitored again. The conversion curves are shown in Figure 3. Clearly catalysts (**5c-f)** are close to exhaustion but remarkably the performance of (**5a**) and (**5b**) are similar to that seen in run 5. Throughout all the monitored reactions (runs 5 and 10) the level of oct-l-ene isomers detected was very low (<1%) and this is at least good circumstantial evidence that the level of Pt leaching is also low. Certainly any Pt species that are leached are relatively catalytically inactive. Catalysts (**5a)** and (**5b**) therefore display a remarkable balance of activity, stability and selectivity.

CONCLUSIONS AND FURTHER WORK

This study has confirmed earlier data [29] that macroporous polystyrene resin-supported Pt complexes form the basis of excellent heterogeneous alkene hydrosilylation catalysts. Reactions can be performed at ambient temperature

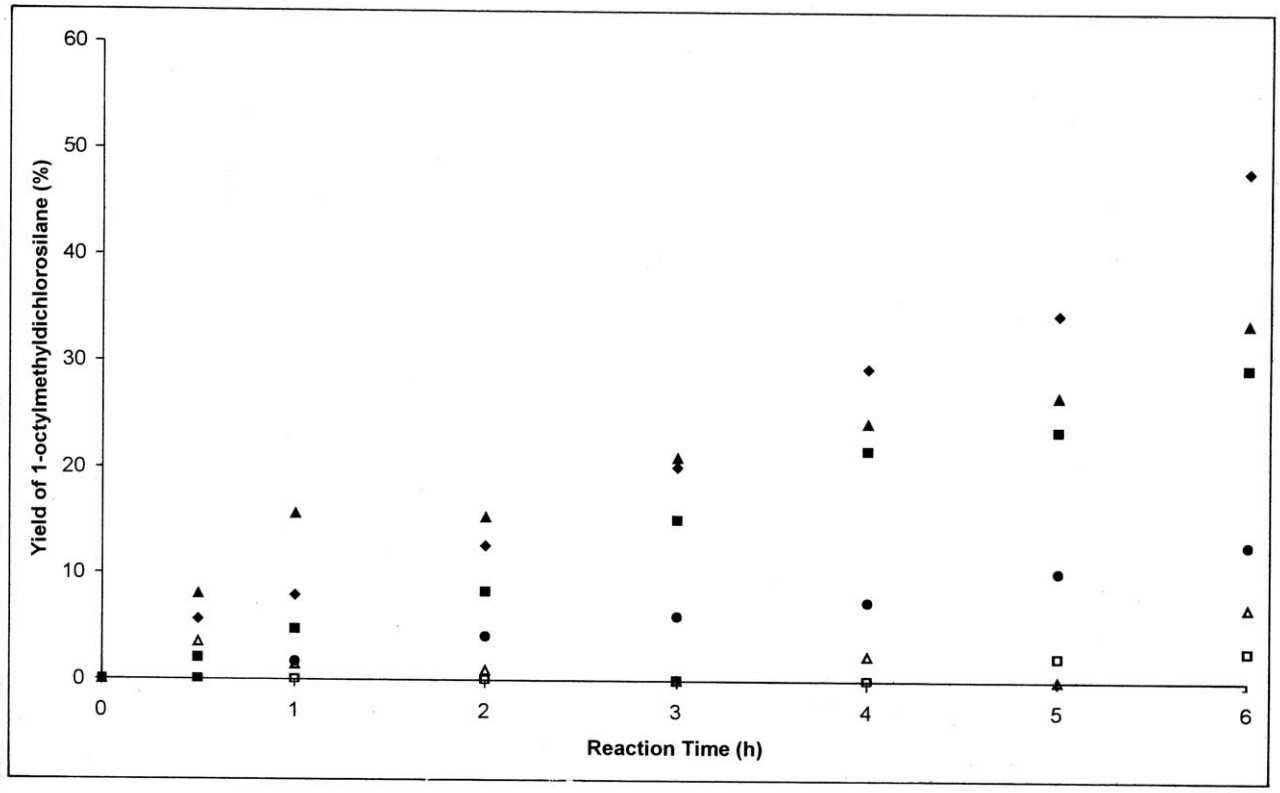


Fig. (1). Room temperature hydrosilylation of oct-l-ene by methyldichlorosilane catalysed by resin supported Pt complexes (oct-l-ene: silane: Pt = 2:1:1 x 10^{-3} **fifth** use of catalyst samples): (**4a**), ◆; (**4b**), ▲; (**4c**), ■; (**4d**), ●; (**4e**) Δ; (**4f**), .

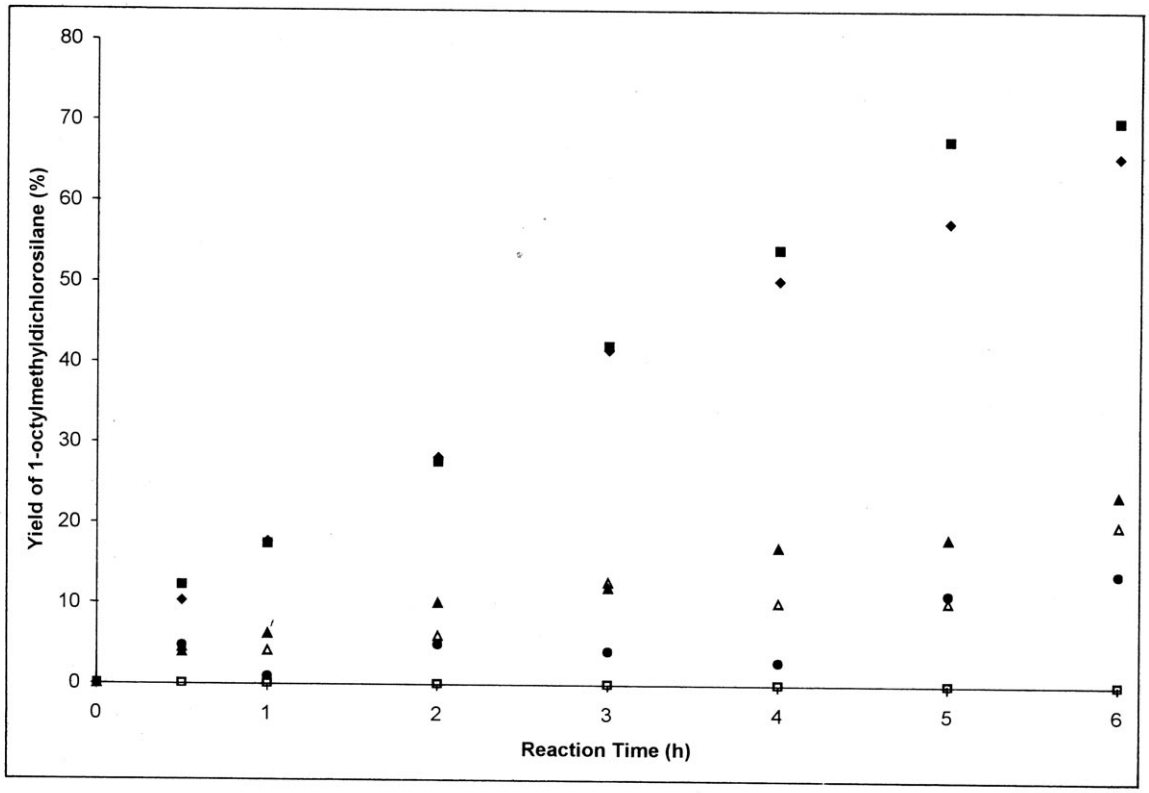


Fig. (2). Room temperature hydrosilylation of oct-l-ene by methyldichlorosilane catalyst by resin-supported Pt complexes (oct-l-ene: silane: Pt = 2:1:1 x 10^{-3}, **fifth** use of catalyst samples): (**5a**), ◆; (**5b**), ▲; (**5c**), ■; (**5d**), ●; (**5e**) Δ; (**5f**), .

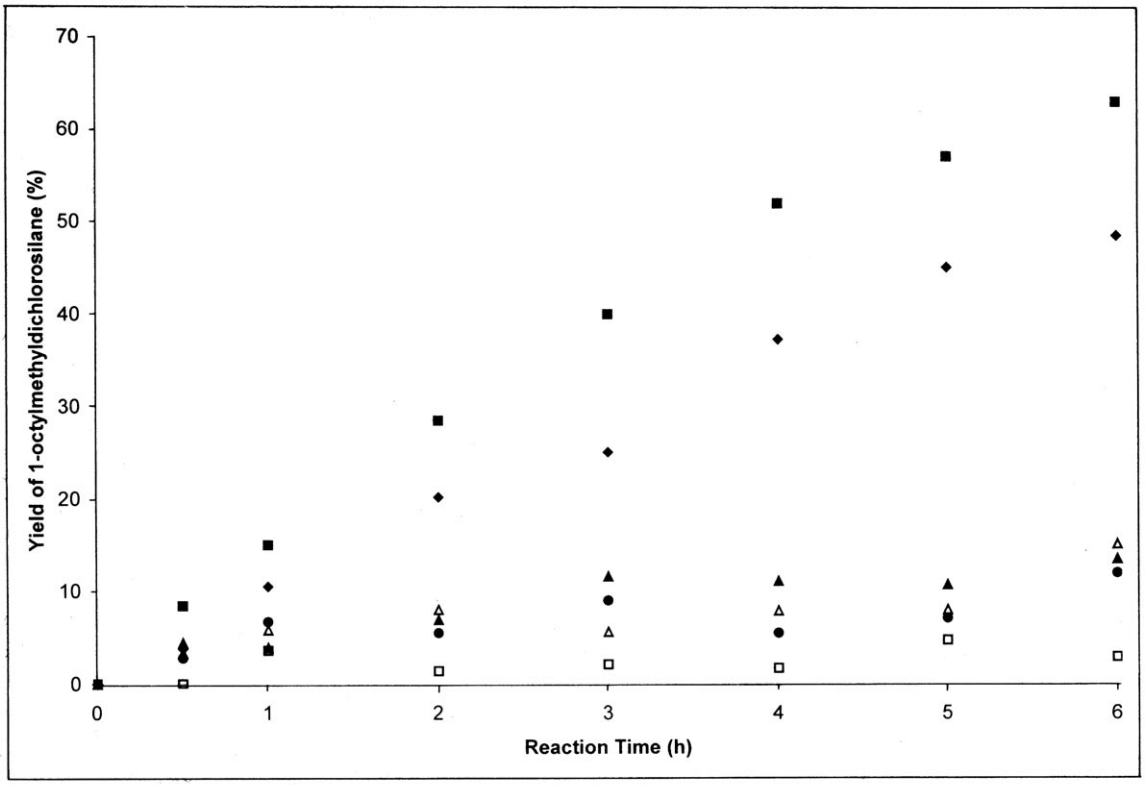


Fig. (3). Room temperature hydrosilylation of oct-l-ene by methyldichlorosilane catalysed by resin-supported Pt complexes (oct-l-ene: silane: Pt = 2:1:1 x 10^{-3}, **tenth** use of catalyst samples): (**5a**), ◆; (**5b**), ▲; (**5c**), ■; (**5d**), ●; (**5e**), Δ; (**5g**), .

under solventless conditions and chlorosilanes do not deactivate the catalytic species. Catalytic activity under given conditions (i.e., alkene: silane: Pt ratio) is optimised by employing Pt loadings of ~ 0.4 mmol g^{-1} on resins with high surface area ~ 150 m^2g^{-1}. These species also show very high selectivity, and in particular very low levels of alkene isomerisation. The best catalysts can be used at least 10 times and still retain very useful activity and selectivity. Indeed such catalysts would be good candidates for evaluation in a continuous hydrosilylation process.

Further optimisation work is possible and indeed is underway. Resins with even higher surface area are accessible and the loading of Pt might be increased further. The ligand Pt ratio may also be important in the latter case to ensure that the tendency to leach Pt is not increased simultaneously.

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