Synthesis of spherical particulate polysiloxane resins as catalyst supports

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Spherical particulate polysiloxanes are synthesised for the first time, chemically derivatised and employed as a support in molybdenum(vi) catalysed alkene epoxidation.

The use of polymer supports in organic synthesis is escalating.[1,2] Currently a particularly active area of research is polymer-supported metal complex catalysts,[3] including asymmetric catalysts.[4] In the case of oxygenation reactions thermo-oxidatively stable supports such as polybenzimidazoles[5,6] and polyimides[7,8] are very attractive.

Polysiloxanes also offer potential in this context, and although these species have been used in a membrane form as metal complex catalyst supports[9–13] and some largely silica-based precipitates have been so described,[14] as far as we are aware these materials have never been produced in a spherical particulate form of dimensions suitable for direct and independent use as heterogeneous supports. This work describes our recent synthesis and characterisation of such spherical particulate polysiloxanes.

The synthetic strategy (Scheme 1) involves the suspension polycondensation of a dispersion of a pre-formed silanol S10 or S5 with tetraethoxysilane (TEOS) catalysed by tin(ii) octanoate in an immiscible continuous phase, such as liquid paraffin, ethylene glycol, or water. The product is essentially a spherical particulate crosslinked polydimethylsiloxane elastomer. The reaction is carried out in a thermostatted 250 ml flanged glass parallel-sided reactor with efficient overhead stirring.[5] Typical reaction conditions are summarised in Table 1 using *e.g.* 25 g of S10. Fig. 1 shows an optical micrograph of resin 8. Aggregation of the product and fouling of the stirrer and reactor can be a problem in small-scale suspension polymerisations. None of the stabilisers we examined to minimise this showed any significant effect [*e.g.* resin 3, Akcros Chem. Monolan E80, polyethylene oxide-polypropylene oxide diblock; resins 7 and 8, Dow Corning Siloxane 2-2502, C_{18} trimethoxysilane], and in our standard procedure (*e.g.* resins 1 and 4) we use no stabilising additives in the continuous phase. Yields of beaded product vary typically from 30 to 70%, average particle diameters were *ca.* 50–200 μm and C, H analysis confirmed the organic content to be close to theoretical.

In all cases the resins formed are elastomeric since the glass transition temperature, T_g, of the polydimethylsiloxane constituting the network is −125 °C. Resins 1 and 4 were prepared with mole ratios of silanols (S10 and S5) and TEOS, such that on average a highly uniform network would result with one S10 or S5 residue between each TEOS derived crosslink. Resins 2

Table 1 Synthesis of spherical particulate polysiloxane resins—Reaction conditions

Resin	Polymerisation mixture (mol ratio reactive end groups)	Continuous phase (vol. ratio disp. : cont.)[a]	Stirrer speed/ rpm	Reaction time/h	Reaction temp./ °C
1	S10/TEOS (2:1)	P (1:7)	700	24	70
2	S10/TEOS (1:2)	EG (1:5)	600	48	80
3	S10/TEOS (1:5)	EG (1:6)	300	18	80
4	S5/TEOS (2:1)	P (1:7)	700	24	70
5	DMDMS/TEOS (2:1)	H_2O (1:7)	600	20	70
6	DMDMS/TEOS (2:1)	H_2O (1:7)	400	22	r.t.[b]
7	S5/CMPTMS (1.5:1)	P (1:7)	600	48	70
8	S10/TEOS/TMOSEP (3.6:1:1)	P (1:7)	700	24	70

[a] P = Liquid paraffin, EG = ethylene glycol. [b] r.t. = Room temperature.

and 3 were prepared with higher levels of TEOS in an attempt to produce some degree of homo-polycondensation of the latter, and hence generate some more rigid silica-like domains in the networks. In practice there is little physical difference between resins 1–4 and this may be due to loss of some TEOS into the continuous phase (liquid paraffin) in which it has some solubility. Resins 5 and 6 were prepared using a slightly different strategy involving dimethyldimethoxysilane (DMDMS) condensed with TEOS under hydrolysing conditions (Scheme 2). Water proved to be a convenient continuous phase in this case and the mole ratio for DMDMS/TEOS was chosen in an attempt to achieve a single dimethylsilanoxy residue between all crosslinks. These products proved to be very

Fig. 1 Spherical particulate polysiloxane, resin 4, × 100

$$x \ HO{\Big(}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{\Big)}_n H \ + \ y \ Si(OEt)_4 \xrightarrow[\text{paraffin}]{Sn(O_2CR)_2} \text{polysiloxane network}$$

TEOS

n = 5, S5
n = 10, S10

polysiloxane network

Scheme 1

Scheme 2

emulsion-like owing to the very small particle sizes. The latter approach is related to the procedure described by Yacoub-George *et al.*[15] which yields essentially a silica-based species with a very low level of organic functionality.

Resin 7 was prepared from silanol S5 but with the TEOS crosslinker replaced by chloromethylphenyltrimethoxysilane (CMPTMS) (with adjustment to the molar ratio) in order to generate functionality in the product. The polycondensation was as before and the content of chloromethyl groups was found to be close to the theoretical value (Calc. from Cl: 1.44 mmol CH_2Cl g^{-1}. Found: 1.55 mmol CH_2Cl g^{-1}), the functionality being located on the crosslinks. Resin 8 was prepared from silanol S10 and TEOS but with half of the latter replaced by trimethoxysilyl-2-ethylpyridine (TMOSEP). Again the polycondensation proceeded as before yielding a content of 0.69 mmol of pyridine per g of resin 8 calculated from N% (theoretical content 0.36 mmol g^{-1}). This higher than expected incorporation of TMOSEP may reflect loss of some of the main components S5/TEOS to the continuous phase. In all cases the resins were found to absorb significant levels (typically *ca.* 4 ml g^{-1} resin) of non-polar solvents (toluene, dichloromethane, light petroleum) but very low levels of ethanol and, of course, water. Thermogravimetry (TG) indicates that all the resins are stable in O_2 to well above 200 °C, with 10% mass loss not occurring typically until *ca.* >400 °C. All the resins were unaffected by 2 M H_2SO_4 but in common with the susceptibility of SiO_2 to dissolve in aqueous alkali, these resins also digested readily in 2 M NaOH.

Amination of resin 7 with an excess of trimethylamine in ethanol at room temp. appears to proceed essentially quantitatively (%Cl, theoretical 5.0; found 4.8: %N, theoretical 2.0, found 2.1), whereas the alkylation of resin 8 with excess MeI in toluene was less efficient (%I theoretical 4.3; found 0.9: %N theoretical 0.5, found 0.65). This was a little surprising since toluene swells the resins better than ethanol. However, the content of chloromethylphenyl groups in resin 7 is substantially higher than the pyridine contents in resins 8, and so overall accessibility may be more impaired in the latter case.

Resin 8 was also treated with a 2 molar excess (relative to pyridine residues) of [$MoO_2(acac)_2$] in refluxing toluene. Following exhaustive extraction with toluene and vacuum drying, dark blue (typical of mixed Mo^{VI}–Mo^{VI} species) somewhat aggregated elastomeric beads were recovered. Through we have not been able to demonstrate unambiguously coordination of resin-bound pyridine to Mo, non-functional supports have previously been shown to be unable to retain such complexes on extraction in a Soxhlet.

Alkaline alcoholic digestion of the resin supported Mo complex and analysis of ICP-AAS yielded a Mo content of 0.43 mmol g^{-1}, corresponding to a pyridine ligand:Mo ratio of 1.5:1. This particulate polysiloxane-supported Mo complex turned bright yellow (characteristic of Mo^{VI}) on contact with *tert*-butyl hydroperoxide (*t*-BHP) and showed very high activity and selectivity as a catalyst in the epoxidation of cyclohexene by *t*-BHP, under conditions very similar to those we have used before. Furthermore, the activity was superior to that of soluble [$MoO_2(acac)_2$] used at the same molar level. Very surprisingly, however, the supported catalyst was also more active than our previously reported polybenzimidazole-supported Mo system since it was used at a much lower level (Mo:*t*-BHP 1:450) than we have used previously (Mo:*t*-BHP 1:80).[16] Mo analysis of the supernatant solution from the epoxidation indicated that <0.02% of the Mo was leached from the support and there is little doubt that the major catalytic component is Mo heterogenised on the polysiloxane.

Further details on the synthesis, characterisation and exploitation as catalyst supports of these spherical particulate polysiloxanes will be reported in due course.

Footnote and References

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