Synthesis of functional polyimide beads and use as Mo^{VI} epoxidation catalyst supports

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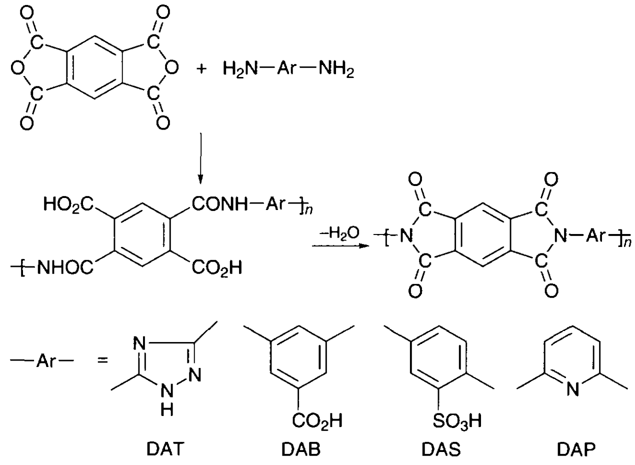
Functional spherical particulate polyimide supports are prepared by a non-aqueous suspension of polycondensation methodology, and one species bearing a triazole residue is used to immobilise a stable and active Mo^{VI} alkene epoxidation catalyst.

Aromatic polyimides probably find the widest range of application among the thermally stable synthetic polymers, and are generally prepared by a two-step procedure[1] from readily available dianhydride and diamine starting materials of low to moderate cost. Formation of poly(amide-acid) solutions, prior to imidisation, provides a very convenient technology for applications as adhesives, sealants and coatings.[2] For application as thermo-oxidatively stable polymer supports,[3,4] however, porous particulate species are required, and we have already reported the synthesis of such materials using relatively mild and easily reproducible procedures.[5,6] Unfortunately, unlike polybenzimidazoles, which are equally thermo-oxidatively stable, simple aromatic polyimides contain no readily exploitable reactive groups, and certainly no inherent donor groups which might act as ligands. They are however much easier to synthesise than spherical particulate polybenzimidazoles[7] and potentially of much lower cost. We have already reported the remarkable performance of a polybenzimidazole-supported Mo^{VI} catalyst in the epoxidation of propane,[8] and we now report the first synthesis of functional spherical polyimides and their use as supports for Mo^{VI} catalysts in cyclohexene epoxidation.



Scheme 1 Schematic Synthesis of Functional Polyimides

The suspension polycondensation procedure adopted has already been reported.[5,6] In this instance the pre-polymer poly(amide-acid) solution in dimethylacetamide–LiCl or *N*-methylpyrrolidone–LiCl was prepared from pyromellitic dianhydride and the functional diamines 3,5-diamino-1,2,4-triazole (DAT); 2,5-diaminobenzoic acid (DAB); 2,5-diaminobenzene sulfonic acid (DAS) or 2,6-diaminopyridine (DAP). Each pre-polymer solution was then dispersed as droplets in liquid paraffin containing poly(maleic anhydride-co-octadec-1-ene) (1 : 1) as a suspension stabiliser, and imidisation induced at 60 °C by addition of a mixture of acetic anhydride and pyridine (Scheme 1). For comparison a non-functional polyimide (PI) was prepared using *p*-phenylene diamine (PDA) and a crosslinked analogue of this (CPI) also produced by inclusion

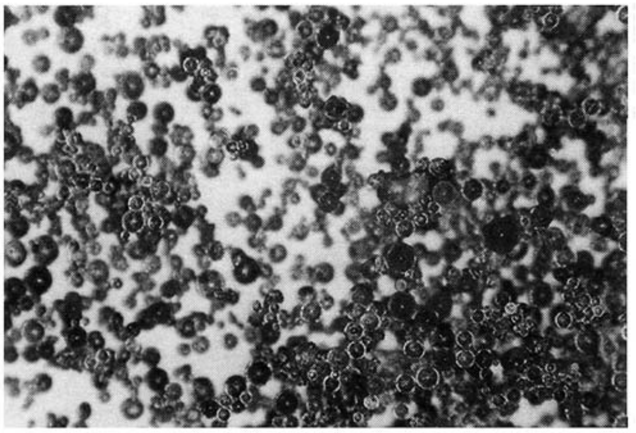


Fig. 1 Optical Photograph of PI-DAS beads (*ca.* 50–500 μm diameter)

Table 1 Elemental microanalytical and particle size distribution data of polyimide particulates

Code	Elemental content											
	Calculated (%)			Found (%)			Particle size fraction (mass%)[a]					
	C	H	N	C	H	N	A	B	C	D	E	F
PI	66.2	2.1	9.7	64.7	3.1	9.0	7.7	2.3	7.1	38.2	44.7	0
CPI[b]	64.2	2.6	10.9	62.2	3.2	10.0	0	28.1	25.3	30.7	12.4	3.5
PI-DAT	58.9	1.6	17.2	45.8	2.9	12.6	0	3.0	5.6	34.8	41.4	15.2
PI-DAB	61.1	1.8	8.4	58.2	3.3	8.9	0	7.4	20.0	33.4	39.2	0
PI-DAS	51.9	1.6	7.5	52.5	3.2	8.1	0	1.5	2.3	3.8	16.0	76.4
PI-DAP	61.9	1.7	14.4	49.7	3.6	9.8	2.4	10.8	7.0	6.9	22.3	50.6

[a] A; < 38 μm, B; 38–75 μm, C; 75–105 μm, D; 106–212 μm, E; 212–425 μm, F; > 425 μm. [b] Crosslinked PI.

of tris(2-aminoethyl)amine (TAA) at a level too low to induced gelling of the pre-polymer. In each case polycondensations were carried out on a 10 or 20 g scale. Most rewardingly none of the functional groups exploited were found to interfere with the polyimide syntheses, and typically 90–100% of mainly spherical polyimide products were recovered after washing and drying[5,6] (Fig. 1). Table 1 shows the results of elemental microanalyses, and the particle size fractionations. Effective combustion analysis of polyimides can be problematical because of their high oxidation stability. In the case of PI-DAT and PI-DAP, the N content found is apparently lower than expected. Additionally the H content of all species is rather high, probably reflecting trapping of solvent, fragments from the dehydrating agents and moisture. The FTIR spectrum of the triazole-containing polyimide (PI-DAT) is exemplary of all the spectra obtained (1780, 1720 cm^{-1}, heterocyclic carbonyl; 1348 m^{-1}, C–N stretch; 720 cm^{-1} imide ring deformation). The thermo-gravimetric analysis (TGA) curves for the particulate polyimides are shown in Fig. 2. The loss of material below *ca.* 300 °C almost certainly corresponds to the physically trapped components mentioned above. Serious degradation of all the functional polyimides in oxygen does not take-off until *ca.* 400 °C. All the materials therefore show good prospects for high temperature application as supports, certainly in reactions up to 300 °C.

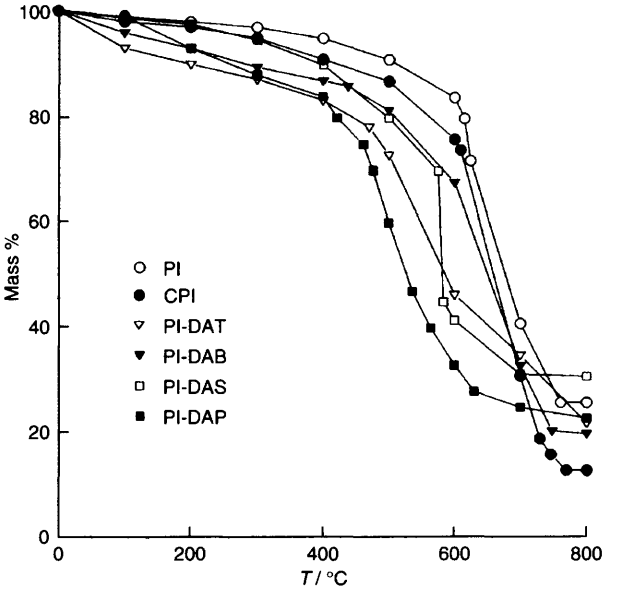


Fig. 2 Thermogravimetric analysis (TGA) curves of functional polyimide beads

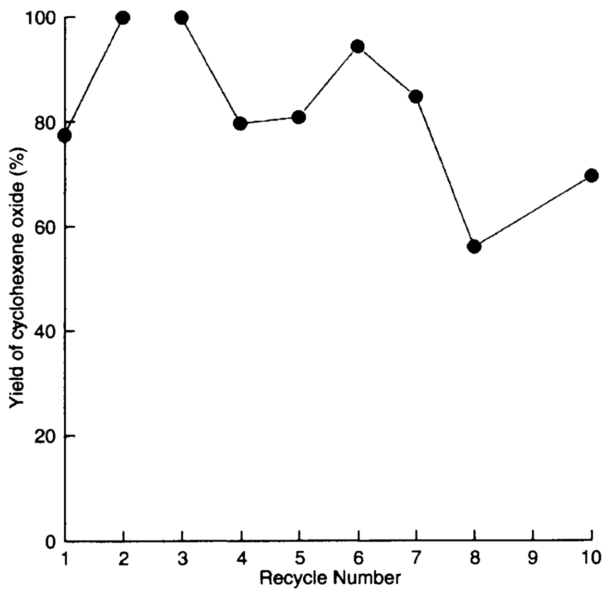


Fig. 3 Recycling of PI-DAT·Mo catalyst in the epoxidation of cyclohexene with *t*BHP (yield at 120 min)

Polyimide PI-DAT was loaded with Mo^{VI} by prolonged refluxing in an ethanol solution of MoO$_2$(acac)$_2$, followed by exhaustive extraction in a Soxhlet. Atomic absorption spectrophotometric analysis indicated a loading of Mo of 2.1 mmol g^{-1}. The PI-DAT·Mo complex was employed as a heterogeneous catalyst in the epoxidation of cyclohexene using *tert*-butylhydroperoxide (*t*BHP), as the oxidant. The conditions were as previously reported[8] [0.08 g polymer catalyst, 7.5 ml (74 mmol) cyclohexene, 2 ml (5 mmol) anhydrous *t*BHP, 60 °C]. The data in Fig. 3 show the yield of cyclohexene oxide (based on 5 mmol *t*BHP = 100%) after 120 min, with the same sample of catalyst recycled 10 times. Although we have previously seen retention of high activity in a polybenzimidazole-supported Mo^{VI} species in the epoxidation of propene,[8] the latter catalyst displayed rather rapid deactivation on recycling in cyclohexene epoxidation.[9] The reported retention of activity by PI-DAT·Mo in cyclohexene epoxidation is therefore most encouraging, and suggests that catalysts based on functional polyimide particulates might form the basis of a range of stable polymer-supported metal complex catalysts, where the support is readily synthesised and is highly cost-effective. Application on both a laboratory and a technical scale also seem feasible.

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