Macromolecular materials in heterogeneous catalysis: an aluminium silasesquioxane gel as active catalyst in Diels–Alder reactions of enones

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A highly active, genuinely heterogeneous catalyst for liquid-phase Diels–Alder reactions of enones results from the silanol centred modification of an incompletely condensed silasesquioxane with trimethylaluminium, the resulting catalytic material being a gel that contains aluminium(III) siloxy functions (Al–O–Si) which are incorporated in a well defined, three-dimensional SiO framework.

At present, silasesquioxane metal complexes can be considered as the best chemical models for a variety of silica supported metal catalysts.[1] In addition, porous materials have recently been synthesized from silasesquioxane cage precursors,[2] as well as metal-containing polymeric derivatives.[3] As such, this field has matured to the extent where applications to *heterogeneous* catalysis may become feasible. Here we report on the formation of an inorganic gel from a silasesquioxane and an organoaluminium precursor. The resulting gel is a highly active, heterogeneous catalyst for liquid-phase Diels–Alder reactions of enones. This paper, therefore, expands the scope of silasesquioxane chemistry to the area of heterogeneous catalysis.

The silasesquioxane **1** (Fig. 1) provides an useful bifunctional building-block for the construction of organosilicious polymeric materials. In **1**, two hydroxy groups occupy '*exo*' positions above interconnected Si_4O_4 rings, which are part of a three-dimensional Si_8O_{11} skeleton. Because of the spatial restrictions of the silasesquioxane skeleton, silanol centred reactions of **1** with bi- and multi-functional organometallics are likely to give polymeric complexes through formation of bridging metal siloxy units. Recently, functionalisations of **1** have been reported that proceed *via* clean silanol centred reactions and that leave the silasesquioxane skeleton intact.[4–6]

We found that, in toluene, the silanol groups present in **1** easily react with trimethylaluminium (Scheme 1), resulting in concomitant formation of methane and a colourless aluminosilasesquioxane gel **2** that occludes the entire volume of the solvent used (*ca.* 50 ml g^{-1}). Upon drying *in vacuo*, the gel collapses into a powder, losing all solvent. The swelling capacity of the dried aluminosilasesquioxane gel **2** for toluene is reduced to approximately 0.5 ml g^{-1}.

When the aluminosilasesquioxane gel **2** is subjected to hydrolysis followed by organic work-up, the silasesquioxane **1** can be recovered in near to quantitative yield (Scheme 1). From this finding, it can be concluded that gel **2** contains a silasesquioxane cage framework similar to that present in the precursor **1**.

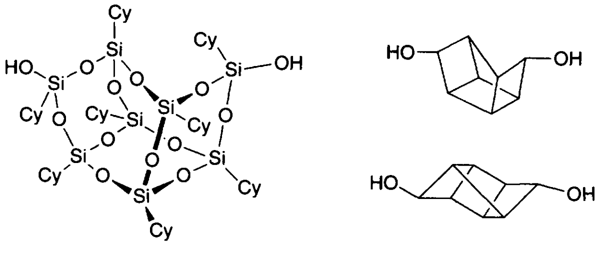
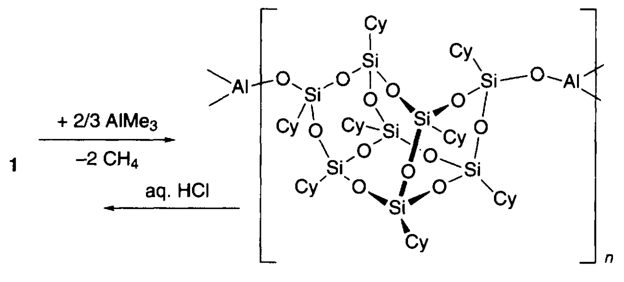


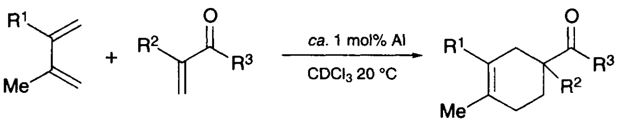
Fig. 1 Structure of the silasesquioxane building block **1** (left) together with schematic representations (right) of the silasesquioxane skeleton, the corners represent cyclohexylsilicon units, the connecting lines represent bridging oxygen atoms; Cy = C_6H_{11}

Analysis of the aluminosilasesquioxane gel **2** by single pulse 79.5 MHz ^{29}Si MAS NMR provides a method to establish the degree of silanol functionalisation. Upon substitution, the originally lower field resonance of the silanol silicon atoms at δ −58.9 shifts towards the higher field part of the spectrum where the other silasesquioxane silicon resonances are also found (δ −65 to −75). Comparison of the integrals over the two distinct parts of the spectra indicates that the fraction of remaining silanol units in the aluminosilasesquioxane gel **2** is <0.05 (*cf.* 0.25 in the silasesquioxane **1**), *i.e.* $>$ 80% of the silanol units of the starting material **1** have been functionalised in the gel forming process. The 104.2 MHz ^{27}Al MAS NMR spectrum of **2** consists of three, partially resolved resonances at δ 50.0, 29.9, and −1.7 ($w_{1/2} \approx 2500$ Hz), characteristic of respectively four, five, and six-coordinate aluminum siloxy units.[7]

The aluminosilasesquioxane gel **2** can be considered as a polymeric Lewis acid. Therefore, we have tested gel **2** as a catalyst for Diels–Alder reactions of enones (Scheme 2). Using **2**, liquid-phase catalytic reactions were conducted in a glass batch reactor at 20 °C. In a typical reaction, 2.0 mmol of diene and 2.0 mmol of dienophile were reacted over the catalyst (1 mol% Al with respect to the substrates) in the presence of $CDCl_3$ as solvent. Some of the results obtained are listed in Table 1. The catalyst employed here accelerates Diels–Alder reactions by several orders of magnitude over the thermal reaction. Moreover, we found that the non-catalysed reactions proceed with formation of up to 30% of 3,4-dihydropyranes, resulting from homo-Diels–Alder reactions of the enones. When the catalyst is filtered off, which was repeatedly done when reactions had reached *ca.* 50% conversion, the reaction rate decreases to the thermal rate. From this finding, we conclude that **2** is a truly heterogeneous catalyst.



Scheme 1 Synthesis of the aluminosilasesquioxane gel **2**; Cy = C_6H_{11}



Scheme 2

Compared to other Lewis-acidic catalysts useful for Diels–Alder transformations, both homogeneous[8] and heterogeneous, the aluminosilasesquioxane gel described here has, at least for the studied reactions, an activity and lifetime that is comparable to the best reported catalysts known to date. With regard to the heterogeneous catalysts, good results have been reported with silica and alumina supported Lewis acids, which are in some way related to the aluminosilasesquioxane described here.[9-12] In addition, zeolites are also successfully employed in this field.[13,14]

In summary, it has been demonstrated that incompletely condensed silasesquioxanes are convenient building blocks for the construction of aluminium containing gels. The resulting materials can be successfully employed as genuinely heterogeneous catalysts in liquid-phase reactions.

Table 1 Diels–Alder reactions catalysed by the aluminosilasesquioxane gel **2**[a]

R^1	R^2	R^3	t^b/h	Isomer ratio[c]	$k_2{}^d$/ l mol^{-1} h^{-1}	$k_2/k_{2(\mathrm{thermal})}{}^e$
H	H	Me	4.5	88:12[e]	0.30	6.1×10^2
Me	H	Me	4.5		0.97	3.2×10^2
H	H	H	3.5	95:5[f]	1.4	6.4×10^2
Me	H	H	1.5		3.0	8.8×10^2
H	Me	H	20	91:9[f]	0.22	2.5×10^3
Me	Me	H	10		0.4	2.1×10^3

[a] Reactions were performed using equimolar amounts (2.0 mmol) of diene and dienophile in $CDCl_3$ at 2.0 mol dm^{-3} concentration at 20 °C in sealed vials that were magnetically stirred using 34 mg (1 mol% Al) of catalyst **2**. Conversions and yields were determined by GC–MS and ^{1}H NMR using an internal standard (*tert*-butylbenzene). [b] Time for 90% conversion. [c] Ratio of 1,4- *vs.* 1,3-disubstituted cyclohexenes. [d] k_2 refers to the average reaction rate measurement. [e] Thermal reactions proceed with formation of up to 30% of 3,4-dihydropyranes resulting from homo-Diels–Alder reactions of the enones. [f] Isomer ratio of the thermal reaction is 71:29. [g] Isomer ratio of the thermal reaction is 75:25.

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