The Use of a High Surface Area Silicon Oxynitride as a Solid, Basic Catalyst

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High surface area silicon oxynitride is shown to be a basic catalyst through its ability to catalyse Knoevenagel condensations when suspended in toluene at 50 °C; the activity is due to the presence of surface nitrogen.

Silicon oxynitride is shown to be capable of acting as a solid, basic catalyst. This is of interest because, (i) it extends the range of inorganic solids that find application as heterogeneous catalysts, such materials being mainly represented by oxides, and (ii) catalysis by solid bases, while less developed than catalysis by solid acids, is of growing importance.[1-3]

The application of non-oxide ceramics in catalysis is facilitated by their increasing availability in high surface area forms,[4] and by surfaces that are kinetically stable to oxidation and hydrolysis. We have previously described the synthesis of a high surface area silicon oxynitride.[5] The presence and stability of surface nitrogen[6] suggested that the surface might show basic properties; some evidence for the presence of basic sites on the surface of silicon nitride was provided by IR spectroscopy in conjunction with the use of probe molecules.[7] To test the possibility of basic catalysis we have investigated the Knoevenagel condensation over silicon oxynitride. This reaction, illustrated in eqn. (1), is usually catalysed by amines in which the nitrogen functions as a basic site.

$$PhCHO + CH_2(CN)CO_2Et \rightarrow$$
$$PhCH{=}C(CN)CO_2Et + H_2O \quad (1)$$
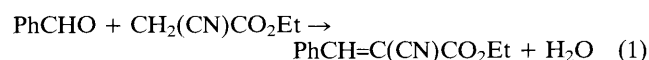
Initial experiments were carried out in toluene (25 ml) at 50 °C with 0.5 g of silicon oxynitride [23 %wt. surface nitrogen, determined by X-ray photoelectron spectroscopy (XPS); 155 m^2 g^{-1}] and 10 mmol of each of the reactants depicted in eqn. (1). The conversion was measured by GLC and confirmed by ^{1}H NMR measurements. After 4 h the conversion to the product was 89%; 70 h 97%. Addition of more reactants (10 mmol) showed that the catalyst maintained its activity, giving 97 and 90% conversions after second and third experiments of 20 h each. After these three experiments

the total number of product molecules formed per unit of surface area was 230 nm^{-2}, clearly indicating a catalytic process. The surface area had decreased only very slightly, to
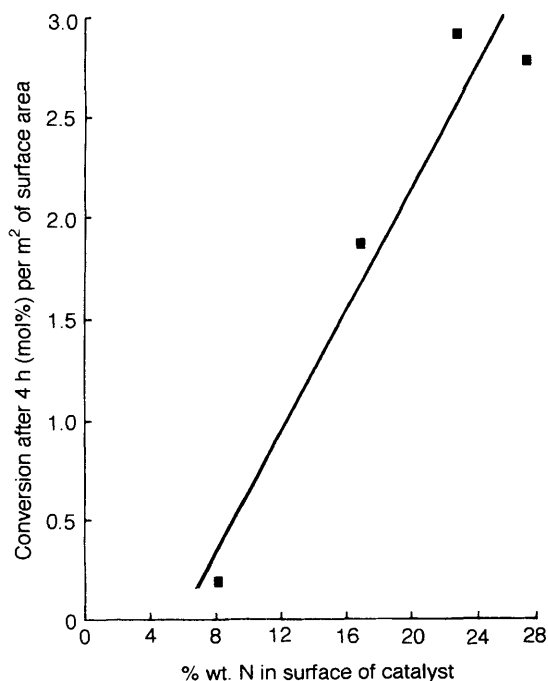

Fig. 1 The activity of silicon oxynitride catalysts in a Knoevenagel condensation as a function of surface nitrogen concentration

Table 1 Comparison of the catalytic activities of silicon oxynitride (SiON) and ammonia in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate in various solvents[a]

Solvent	Catalyst	Product formed after (%)	
		4 h	20 h
Toluene	SiON	85	100
Toluene	Ammonia	5	25
Ethanol	SiON	65	95
Ethanol	Ammonia	90	100
THF	SiON	15	[b]
THF	Ammonia	10	45

[a] Reactions carried out in 30 ml solvent at 50 °C using 0.2 g SiON or 0.4 mmol gaseous ammonia (9 ml under ambient conditions) injected into the solution, and 4 mmol of each reactant. The term 'SiON' is a convenient abbreviation for silicon oxynitrides containing varying N : O ratios; in these experiments the SiON used contained 28 % wt. N (measured by XPS) on the surface, had a surface area of 185 $m^2 g^{-1}$ and was evacuated at 50 °C for 1 h before reaction. THF, tetrahydrofuran. See eqn. (1) for the reaction. [b] 17% conversion based on reactants, 2% based on product.

130 $m^2 g^{-1}$, and the N : Si atomic ratio in the surface of the solid, measured by XPS, had decreased from 0.9 to 0.7. Samples of silicon oxynitrides from various preparations, with differing surface areas and surface nitrogen contents, could be used as catalysts. The specific activity of such catalysts, defined as the conversion attained after 4 h in the above Knoevenagel condensation reaction divided by the surface area of the catalyst present in the reaction, was found to correlate with the amount of nitrogen on the surface (Fig. 1).

Further support for the conclusion that the observed activity is specific to the presence of nitrogen in the surface is provided by the findings that neither silica (Aerosil; 0.5 g; 300 $m^2 g^{-1}$) nor mesoporous silicon carbide[6] (0.5 g; 172 $m^2 g^{-1}$; 42 atom% surface carbon) are active as catalysts under the above conditions.

In the reaction of benzaldehyde with malonitrile, a conversion of 90% was reached after 4 h, in toluene; in the reaction of cyclohexanone with ethyl cyanoacetate the conversion was 80% after 20 h, in ethylbenzene. Both reactions were carried out at 50 °C using 0.5 g of a silicon oxynitride (17 % wt. surface N; 141 $m^2 g^{-1}$) and 10 mmol of each reactant.

The effect of some solvents on the reaction is shown in Table 1, both with silicon oxynitride and with dissolved, gaseous ammonia as catalysts. The silicon oxynitride exhibits comparable activities in toluene and ethanol. Dissolved ammonia is highly active in ethanol, presumably due to the generation of ammonium ethoxide, moderately active in THF and only slightly active in toluene (solubility of ammonia in toluene is 0.3 at 20 and 0.16 mol dm^{-3} at 50 °C; the latter concentration is eight times higher than that used in the experiments of Table 1). Unexpected solvent effects have also been found in Knoevenagel condensations catalysed by calcium silicate.[8]

The possibility that the observed activity is due to ammonia in solution, derived from the silicon oxynitride, is unlikely for the following reasons. First, in the experiments in which the silicon oxynitride catalyst was re-used, the catalyst was separated from the solution by filtration after the three experiments described above; fresh reactants were added to the filtrate but no conversion took place over 20 h at 50 °C. Secondly, the data of Table 1 show that the relative reactivity of SiON in toluene, ethanol and THF is qualitatively different from the reactivity of ammonia in these solvents, and there is no obvious way to explain these differences if it is assumed that the SiON functions by release of ammonia. Thirdly, a thermogravimetric analysis of a silicon oxynitride shows a weight loss of less than 0.1% up to 1000 °C. This means that there is less than 0.06 mmol ammonia per g silicon oxynitride that can be readily desorbed; comparison with the data of Table 1 indicates that this is too small an amount to be responsible for the observations.

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