Reichardt's dye as a probe for surface polarity of chemically and thermally treated silicas

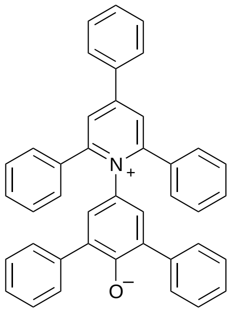
Stewart J. Tavener, James H. Clark,* Gary W. Gray, Paul A. Heath and Duncan J. Macquarrie

Department of Chemistry, University of York, Heslington, York, UK YO1 5DD

The polarity of surfaces may be conveniently estimated by measuring the energy of the π ⟶ π* transition of adsorbed Reichardt's dye.

Surface polarity strongly affects the ability of material surfaces to adsorb compounds, which may in turn affect many useful properties of solids including catalytic activity. In heterogeneous catalysis, the reaction occurs either at the catalyst surface, inside pores, or in the slow moving liquid film at the surface (Nernst layer). The adsorption of substrates and the desorption of products are important steps in heterogeneous catalytic processes and are often rate limiting.[1] In certain cases, such as supported phase-transfer catalysts, the compatability of the surface with the reactant phases is critical.[2] However, measuremants of surface polarity are not easy and are rarely used in practice.

Reichardt's dye (**I**) is a useful indicator of solvent polarity.[3]



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It is strongly solvatochromic, and shows a range of energies for its π ⟶ π* absorption band from 147 kJ mol^{-1} (810 nm) in diphenyl ether to 264 kJ mol^{-1} (453 nm) in water. Solvent polarity is measured simply by recording the energy of the π ⟶ π* transition in kJ mol^{-1}. This may be normalised to avoid non-SI units [eqn. (1)].

$$E_{\mathrm{T}}^{\mathrm{N}} = \frac{E_{\mathrm{T(solvent)}} - E_{\mathrm{T(TMS)}}}{E_{\mathrm{T(water)}} - E_{\mathrm{T(TMS)}}} \qquad (1)$$

Reichardt's dye immobilised on silica gel has recently been reported as being a sensitive optical chemical sensor, giving significant shifts in $\lambda_{\max}$ when the liquid environment of the sensor was changed, although these shifts were smaller than those seen for the free dye in solution.[4] Reichardt's dye doped organic polymers have been used as optical sensors for humidity, gaseous ammonia, and for polar additives in hydrocarbon blends.[5]

Some attempts have been made to measure solvatochromic parameters for the surfaces of inorganic oxides, but these investigations have usually involved the study of the solid in contact with a mobile liquid phase.[6] Silica samples studied as a suspension in 1,2-dichloroethane were found to have an $E_{\mathrm{T}}^{\mathrm{N}}$ value of 0.798 to 0.842,[7] and were also found to have extremely high polarities as measured by the UV adsorption maximum of adsorbed 4-nitroanisole.[8] Reichardt's dye has been used to demonstrate that dry alumina surfaces have a greater polarity than bulk water.[9]

We now wish to report that Reichardt's dye will also act as a convenient probe for the polarity of surfaces of chemically and thermally treated silica surfaces. A solution of the dye (in dichloromethane) is simply added to the the material under study, the solvent removed on a rotory evaporator and the material dried on a vacuum line for 10 min, after which no residual dichloromethane could be detected on the material by DRIFTS. Care must be taken to avoid overloading the surface with dye, as dimerisation is known to occur in solution at higher concentrations: the amount of dye added was therefore restricted to 1 μmol g^{-1} (*ca.* 2 nmol m^{-2}).[9] The choice of solvent used to download the dye is critical: alcohols and ketones will react with or bind strongly to surface hydroxy groups on silica surfaces,[10] and the dye is insufficiently soluble in apolar solvents such as aliphatic hydrocarbons. THF also proved troublesome as high peroxide concentrations caused bleaching of the dye. Dichloromethane was found to be the most suitable solvent by virtue of its high volatility and chemical stability. The π ⟶ π* transition energy of the adsorbed dye is measured by diffuse reflectance UV–VIS spectrophotometry, although the polarity may be estimated by eye: very polar surfaces such as untreated silicas are red, ranging through purple and blue for organosilicas, to green for non-polar surfaces such as macroporous polystyrene. The values for $E_{\mathrm{T}}^{\mathrm{N}}$ presented here are calculated using a modified version of eqn. (1), using $E_{\mathrm{T(surface)}}$ instead of $E_{\mathrm{T(solvent)}}$.

The dye may not be used in strongly acidic environments as the oxygen centre becomes protonated, preventing the solvatochromic transition.[11] Residual adsorded HCl prevents sensible values from being obtained for the surface polarities of silicas treated with chlorosilanes.

A range of thermally treated silicas were prepared by heating commercial mesoporous silicas (Kieselgel 60 and Kieselgel 100, *ex Merck*) for 20 h at the desired temperature under a flowing nitrogen atmosphere before being treated with the dye solution. Thermal dehydration of silica gel is known to have a

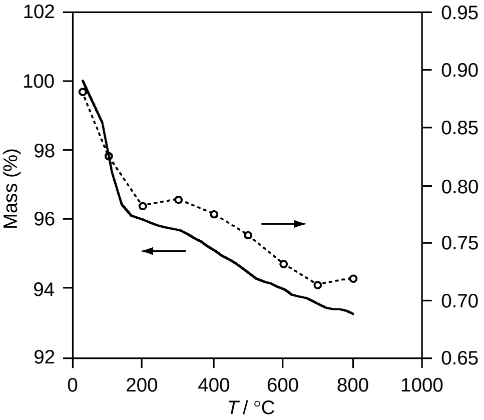


Fig. 1 Thermogravimetric analysis and the effect of thermal treatment on the polarity ($E_{\mathrm{T}}^{\mathrm{N}}$) of Kieselgel 60 silica

large effect on surface chemistry of the silica, but comparatively little effect on its surface area: heating silica to 810 °C will decrease the surface area by only 25%, but will decrease the concentration of surface hydroxy groups by 80%.[12] Thermal treatment of both silicas was found to have a marked effect on its polarity, with the E_T^N value reflecting thermogravimetric analysis data (Fig. 1). Initial heating causes a rapid loss of mass as loose, physisorbed water is removed from the surface, and a decrease in polarity as the adsorbed dye is no longer in a wet 'supported water' environment, but now sees a hydrogen-bonded network of surface silanols.[10] Further heating will remove some of these silanols, producing isolated polar groups whose polarity is not mediated by hydrogen bonding, this is reflected in the slight increase in polarity observed in the 300–400 °C region for both silicas. As the temperature is raised to 700 °C, more surface hydroxy groups react, eliminating water and producing more and more siloxane bridges (Fig. 2). Both silicas show an increase in polarity on heating beyond 700 °C. The cause of this is not clear but may be due to a low energy restructuring of the gel matrix, although no energy changes could be detected by differential scanning calorimetry. The temperature is lower than the quartz–tridymite phase change for crystalline silicas, which occurs at 870 °C.[10]

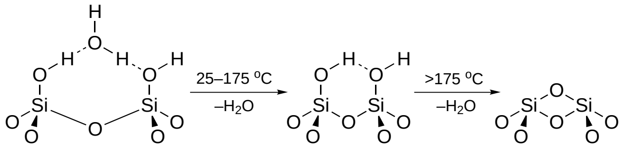


Fig. 2 Thermal dehydration of a silica surface

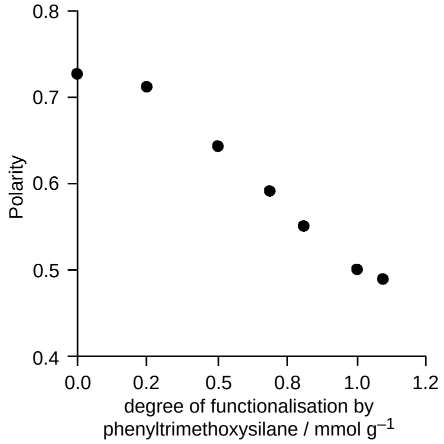
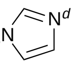


Fig. 3 Effect of the degree of functionalisation on the polarity (E_T^N) of silicas treated with phenyltrimethoxysilane

Table 1 Polarities of a range of organically modified silicas

Material[a]	Degree of functional-isation[b]/ mmol g^{-1}	λ_{max}/nm	E_T^N	ΔE_T^N/ mmol^{-1} g
Silica–OH[c]	—	477	0.967	—
Silica–$OSiMe_3$	0.53	560	0.630	−0.634
Silica–Ph	1.00	610	0.500	−0.467
Silica–$(CH_2)_3Cl$	0.64	554	0.645	−0.503
Silica–$(CH_2)_3NH_2$	0.99	590	0.546	−0.425
Silica–$(CH_2)_2CN$	0.99	557	0.636	−0.334
Silica–$(CH_2)_3N$  N[d]	0.97	611	0.497	−0.485
Polystyrene[e]	—	752	0.225	—

[a] Prepared by reaction with the appropriate organosilane, unless otherwise stated. [b] Measured by C, N elemental microanalysis. [c] Kieselgel 100, untreated. [d] Imidazole functionalised silica; for preparation method see ref. 14. [e] Amberlite XAD4 macroporous polystyrene.

Silicas chemically modified by reaction with organosilane reagents such as phenyltrimethoxysilane show a reverse linear correlation between degree of functionalisation and polarity as measured by the E_T^N values (Fig. 3). For these materials the dye is exposed to greasy non-polar organic functions as well as fewer polar surface hydroxy groups, compared with the unmodified silica. The measured polarities of a range of organically modified silicas at specific degrees of functionalisation are given in Table 1. There was no observable change in the IR spectra of the various materials after absorption of the dye, although it should be noted that the dye is present in quantities approximately 1000 times smaller than those of the surface bound organic groups, and is below the limits of detectability by IR.

Although all of the organic groups studied reduce the polarity of silica, they do so by different degrees. The decrease in polarity per mmol of organic groups per gram of silica (ΔE_T^N) increases in the order: cyanoethyl < aminopropyl < imidazole < phenyl < chloropropyl < trimethylsiloxyl which is broadly in agreement with the E_T^N values found for comparable compounds in the liquid phase: TMS = 0.000, benzene = 0.111, 1-chlorobutane = 0.191, *n*-butylamine = 0.213, propionitrile = 0.401, water = 1.00.[13]

Adsorption of Reichardt's dye on chemically and thermally treated silicas is an easy and rapid method for reliably determining the polarity of surfaces. This method should prove to be a valuble technique in the study of adsoption and desorption in liquid/solid catalytic systems.

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Footnote

* E-mail: jhcl@york.ac.uk

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