The use of Reichardt's dye as an indicator of surface polarity

Duncan J. Macquarrie,*[a] Stewart J. Tavener,[a] Gary W. Gray,[a] Paul A. Heath,[a] John S. Rafelt,[a] Sylvie I. Saulzet,[a] Jeff J. E. Hardy,[a] James H. Clark,[a] Pierre Sutra,†[b] Daniel Brunel,[b] Francesco di Renzo[b] and Francois Fajula[b]

[a] *Department of Chemistry, University of York, Heslington, York, UK YO10 5DD*
[b] *Laboratoire des Matériaux Catalytiques et Catalyse en Chimie Organique, CNRS UMR 5618, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'Ecole Normale, 34296 Montpellier cedex 5, France*

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Reichardt's dye can be used to determine the surface characteristics of a range of inorganic and organic materials. This simple, rapid technique gives information regarding the polarity of the surface.

1 Introduction

The characterisation of solid surfaces is of vital importance to many areas of chemistry, including heterogeneous catalysis, chromatography and separation, and adsorption. Many techniques are available to study solids, some of which are, to some extent at least, surface specific. These include spectroscopic methods such as IR spectroscopy (with or without probe molecules such as pyridine to investigate specific types of sites), (CP) MAS NMR (which can be used to determine the connectivities of *e.g.* silicon atoms at the surface of *e.g.* zeolites and silicas) and EPR,[1,2] which is of use in materials containing unpaired electrons. Thermal techniques can also be used to probe the strength of interaction of probe molecules with surfaces. These techniques include temperature programmed desorption (TPD), in which probes such as ammonia and carbon or sulfur dioxide can be used to determine the strength of interaction of acidic and basic sites respectively, and microcalorimetry, which typically uses water as a probe molecule, and which has been used to determine the hydrophobicity/hydrophilicity of silica surfaces.[3] The strength of interaction occurring during molecular adsorption on a solid surface mainly depends on the dipole–dipole, hydrogen-bonding and charge transfer interactions of the molecule with the surface. These various interactions of a given adsorbate with solid surfaces are connected with the surface affinity. In most cases the latter property can be expressed by the term surface polarity. Hence, the measurement of such a term is of great significance.

The measurement of surface polarity is of great significance in the characterisation of solids, particularly adsorbents and catalysts, where the adsorption/desorption behaviour is of great importance.[4] In certain cases, such as supported phase transfer catalysts, compatibility of the reactant and the surface is critical.[5,6] However, measurements of surface polarity are not easy, and are rarely used in practice.

The use of solvatochromic indicators is widespread in the determination of solvent parameters such as polarity and polarisibility, Lewis acid/base character and H-bonding donor–acceptor character. One of the most useful of these is the betaine **1**, known as Reichardt's dye.[7,8] This molecule has a charge transfer transition in the visible region, which is very medium dependent, and is principally due to differential stabilisation of the charge separated ground state, although stabilisation of the excited state is also relevant (Fig. 1).

The range of transition energies is extremely large, from 263.8 kJ mol^{-1} (453 nm) for water to 147.1 kJ mol^{-1} (882 nm) for tetrachloromethane. This probe molecule has been used for a great number of solvents,[7,8] and chromatographic stationary phase/solvent mixtures.[9-12] We have recently published a preliminary communication which describes the use of **1** as a quick and effective probe of surface polarity in some inorganic solids.[13,14] We now present our findings on the scope and limitations of the technique in a variety of systems. In this respect, various materials have been studied including mineral oxides and organic polymers. Special attention has been focussed on organic–inorganic hybrid materials which are the subject of intense interest at the current time. These materials were prepared by two different procedures: either by covalent anchoring of organic moieties through surface silanation of the mineral support, in this case either commercial silica gel or micelle templated silica (MTS) materials, or by *in situ* preparation of organically modified hexagonal mesoporous silica (HMS).

2 Experimental

2.1 Materials

Reichardt's dye **1** was purchased from Aldrich and used as received. All solvents were AR grade, and were not further

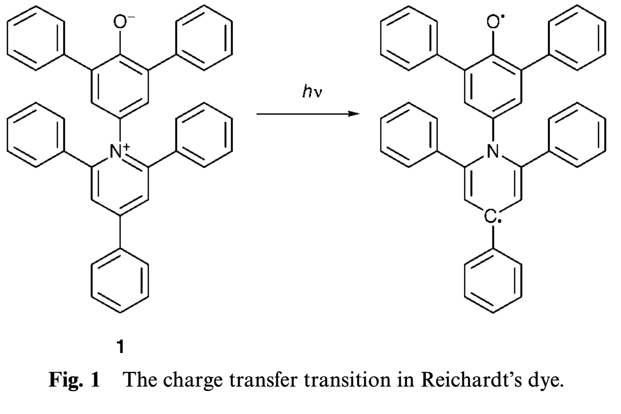

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Fig. 1 The charge transfer transition in Reichardt's dye.

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† *Present address:* Dipartimento di Chimica 'G. Ciamician', Laboratorio di Photochimica, Universita di Bologna, 40126 Bologna, Italy.

purified. All other materials were commercial samples from lab suppliers, details of which are given in the text.

2.2 Hexagonal mesoporous silica (21A-HMS)[15]

Decylamine (0.0054 mol) was added to a solution of deionised water (11.8 mol) and absolute ethanol (3.6 mol) in a conical flask. The solution was stirred for 20 min and tetraethoxysilane (0.4 mol) was added slowly. A white precipitate formed over a period of 15 min and the resulting mixture was aged for 18 h. The mixture was then filtered and dried on a rotary evaporator, and was finally calcined in air at 873 K for 4 h to remove the template.

2.3 Micelle templated silica (MTS)

This was prepared following a procedure derived from Mobil's original method.[16] 42 g (0.68 mol) of Zeosil 175 MP (Rhone Poulenc) were added to a stirred solution of 22 g (0.2 mol) cetyltrimethylammonium bromide (CTMABr) and sodium hydroxide (6.3 g, 0.16 mol) in 340 ml deionised water. The mixture was then heated in a mechanically stirred autoclave at 393 K under autogenous pressure for 16 h. The solid phase was then filtered off, washed with water (until pH = 7) and then ethanol and dried at 353 K in air. Calcination at 823 K in flowing air for 7 h eliminated the template and yielded the final MTS material.

2.4 Grafting

In a typical grafting process, 3 g of MTS (activated at 473 K under vacuum for 15 h) were treated with the grafting agent (an appropriate organo(trimethoxy)silane, 9 mmol) in refluxing anhydrous toluene for 6 h. Excess grafting agent was removed by Soxhlet extraction (1 : 1 Et_2O–CH_2Cl_2). The grafted material was then dried in air at ambient temperature.

2.5 Trimethylsilyl end-capped materials

1.5 g of pre-activated (348 K under vacuum for 15 h) grafted MTS were treated with 5.25 ml of hexamethyldisilazane (HMDS) in the vapour phase under dynamic vacuum (10 mmHg) at 384 K for 4 h . The material was evacuated for an additional hour at 348 K under vacuum.

2.6 Chemically modified silicas

Silica (10 g) was added to toluene (100 ml). To this stirred suspension was added the appropriate silane (50 mmol), and the mixture heated to reflux. Reflux was continued for 4 h, the resultant alcohol removed by distillation, and the reflux continued overnight. The mixture was allowed to cool, and the solid collected by filtration and washed with toluene (2 × 100 ml), acetone (100 ml), water (100 ml) and finally acetone (2 × 100 ml) before being air dried and then dried at 373 K overnight.

2.7 Chemically modified HMS materials (*in situ* method)[17]

A solution of dodecylamine (5.08 g) in ethanol (46 ml) and distilled water (53 ml) was prepared. To this were added tetraethoxysilane and an organo(trimethoxy)silane in a specified ratio (for a 1.1 mmol g^{-1} loading the ratio is 9 : 1, for 2.4 mmol g^{-1} the ratio is 4 : 1). The mixture was stirred overnight, the solid filtered off, and the template removed by either reflux in ethanol (10 ml ethanol per g of solid) or by Soxhlet extraction with ethanol. The resultant solid was then dried at 373 K.

2.8 Thermal treatment of silica

For the polarity *vs.* thermal treatment experiments, silica was placed in an oven at the desired temperature for 18 h, removed and allowed to cool in a desiccator.

2.9 Preparation of samples for surface polarity measurements

The solid (*ca.* 1 g) was treated with a solution of **1** in dichloromethane (*ca.* 10^{-4} M) at room temperature. The solid typically adsorbs the dye from solution within a few seconds. In some cases no colour changes were observed, whereupon more dye solution was added until the solid had become distinctly coloured. The loading of **1** required to give a distinct colour varied from 0.012 to 0.083 μmol m^{-2} depending on the solid under investigation. It was found that amine containing materials required less dye than neutral materials. In all cases spectra could be achieved over a wide range of loadings, without any change in band shape (due to *e.g.* microcrystallites of dye, such adsorption bands were only seen at very high loadings, typically $\geqslant$0.3 μmol m^{-2}). In order to achieve good quality spectra, the actual dye loading used was therefore significantly above the minimum required. At this point the solvent was removed on a rotary evaporator, to give a free-flowing powder, and then the remaining traces of solvent removed under vacuum (10^{-2} Torr for 2 h). The UV–VIS spectrum of the solid was measured against the unimpregnated solid in a Diffuse Reflectance UV-visible spectrometer. The maximum of the lowest energy (charge transfer) transition was measured, and the E_T^N value calculated as follows

$$E_T\ (\text{kcal mol}^{-1}) = 28591/\lambda_{max}\ (\text{nm}) \qquad (1)$$

$$E_T^N = \frac{E_{T(\text{solvent})} - E_{T(\text{TMS})}}{E_{T(\text{water})} - E_{T(\text{TMS})}} \qquad (2)$$

where E_T is the energy of the charge transfer transition in water [$E_{T(\text{water})} = 32.4$], the solvent (surface) and tetramethylsilane [$E_{T(\text{TMS})} = 30.7$] respectively.

3 Results and discussion

Given the size of the probe molecule, it is unlikely that the technique will be applicable to microporous materials. However, porosity measurements on all the materials discussed here (with the possible exception of the organic polymers, see Section 3.8) indicate that, for all the materials >95% of the surface area exists in mesopores of >2 nm diameter. Given that access to such pores is known for molecules of the dimensions of metal–salen and metal–porphyrin complexes, and that these species themselves are capable of catalysis, we are confident that the dye molecule will readily access the vast majority of the surface of these materials.

3.1 Choice of solvent and loading of dye

The choice of solvent is important for this application, and initial attempts at using the technique suffered from lack of reproducibility, which was later traced to use of inappropriate solvents. Reichardt's dye **1** is soluble in most organic solvents except alkanes and has very poor solubility in water. Two major factors are important in the choice of solvent. A volatile solvent is important, since traces of solvent which remain on the solid can affect the result significantly. Secondly, the solvent must be unreactive under the conditions of the adsorption. Our initial attempts to apply this technique to silicas were carried out in acetone as solvent, and were found to be irreproducible. This was later traced to the fact that acetone can interact strongly with the surface of silica,[18] meaning that the measured polarity did not correspond to the silica surface but rather to a derivatised material containing variable amounts of modified sites. Alcohols are precluded for similar reasons. We have found that of the remaining simple solvents available, dichloromethane is the most generally useful, combining excellent volatility with very low reactivity towards many surfaces.

Line shapes and absorption maxima were identical over a wide range of dye loadings for all the inorganic materials studied. The spectra of dye clusters gives a broad weak maximum at 628 nm, which only becomes apparent at dye loadings of $\geqslant 3$ µmol m^{-2}.

Thus, the peak maxima represent the interaction of the dye with the surface, and not the dye with itself. For the very low surface area materials, especially the organic polymers, dye clustering was a much more severe problem, and microcrystals of dye formed at low coverages, at which the adsorption of interest was still relatively weak. However, it was still possible, with careful control of the quantities of dye adsorbed, to achieve useful results. It is thought that the very low surface areas of the organic materials is the major contributing factor to this phenomenon, and may represent a limitation to the usefulness of the technique.

3.2 Silica

E_T^N values for various silicas and other inorganic materials are given in Table 1. The surface chemistry of silica at different temperatures is relatively well understood, and can, to an approximation, be represented as shown in Fig. 2:

The undried material contains a substantial amount of water (typically *ca.* 10%) and is thus very polar. As the temperature is increased, this loosely bound water is removed, and the underlying hydroxylic surface is exposed. The surface consists predominantly of silanol groups (*ca.* 2.5–4.5 silanols nm^{-2} according to several methods of measurement[1]), most of which are hydrogen bonded to neighbouring silanols. A small fraction are geminal silanols [=Si(OH)$_2$] which are considered to be particularly acidic, owing to the ability of one hydroxy group to H-bond to the other O centre. Removal of the loosely bound water exposes this surface, which is likely to be less polar than the hydrated material. Most of the water present is lost before *ca.* 423 K for mesoporous silicas such as those studied here. Further thermal treatment gradually crosslinks the vicinal silanols, leading to significant amounts of the relatively non-polar siloxane groups on the surface, and a corresponding drop in the number of hydroxy groups. The remaining silanols become increasingly isolated owing to the increasing number of intervening siloxane groups.

Table 1 E_T^N values for a range of inorganic solids

Material^a	Surface area/m^2 g^{-1}	Dye loading/ µmol m^{-2}	λ_{max}/nm	E_T^N
SiO$_2$ (Kieselgel 100)	254	0.04	477	0.967
SiO$_2$ (Kieselgel 60)	425	0.023	483	0.880
Aerosil	272	0.025	527	0.730
HMS21	950	0.045	516	0.764
MTS	980	0.050	512	0.768
Celite	47	0.08	655	0.390
Al$_2$O$_3$ (calcined)^b	32	0.095	630	0.452
Al$_2$O$_3$ (basic)	100	0.09	470	0.93
Al$_2$O$_3$ (neutral)	112	0.09	436	1.07
Al$_2$O$_3$ (acidic)	104	0.09	418	1.16
TiO$_2$	56	0.08	581	0.571
ZrO$_2$^{c}	—	—	—	—

^{a} Silanol densities (refs. 19–23): silicas 2.1–3.3 SiOH nm^{-2}, MTS 2.4 SiOH nm^{-2}. ^{b} Calcined alumina ex Aldrich, no pretreatment. ^{c} Surface may be too acidic, and leads to protonation of dye.

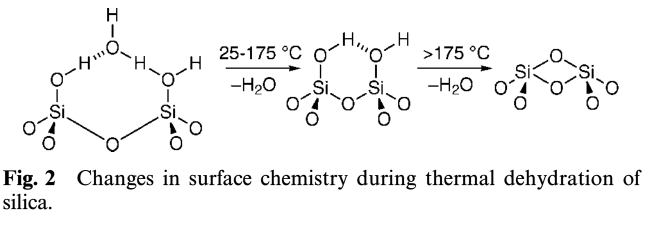

Fig. 2 Changes in surface chemistry during thermal dehydration of silica.

Previous work using Reichardt's dye[9,12,24] on silica–solvent systems indicates that the dye can measure hydrogen bond donor–acceptor and Lewis acid-base properties—*i.e.* the surface sites SiOH, SiOSi and surface defects all influence the behaviour of the dye in solutions in contact with the surface.

Since **1** is known to be very sensitive towards hydroxylic media, the response of the dye to changes in the silica surface induced by thermal treatment should be substantial. Two samples of silica, Kieselgel 100 and Kieselgel 60 were thus subjected to increasingly harsh thermal treatment (18 h in a furnace at temperatures between 373 and 1073 K), allowed to cool in a dessicator, and the sample then treated with **1**. TGA analysis of the dried samples indicated that rehydration was slow enough that only a very small proportion of the water lost during drying would be readsorbed during the sample preparation and data acquisition. A typical spectrum is shown in Fig. 3, which is that of Merck Kieselgel 60 dried at 473 K and with a dye loading of 0.028 µmol m^{-2}. The broken lines represent deconvolution analysis, using Gaussian functions, separating the strong π–π* transition at higher energy from the lower energy charge transfer at 495 nm.

The values for E_T^N obtained are compared with the thermal analysis trace of the sample, obtained with a 10 K min^{-1} heating rate, to simulate the weight loss–temperature relationship (Fig. 4)

As can be seen, the two curves fit extremely well, indicating that **1** is a very useful indicator of the nature of the surface. With wet silica, the E_T^N value is almost that of water in the case of Kieselgel 100, and only slightly lower for Kieselgel 60. As the temperature of pretreatment increases, the polarity drops, initially rapidly, as water is removed, then more slowly as the more demanding crosslinking takes place. The final value which is obtained is 0.72, similar to a lipophilic long chain alcohol. There is a difference in absolute values between the two silicas investigated, but the same pattern is evident. The increase in polarity seen between 973 and 1073 K appears to be real, and not due to experimental error, as it was obtained reproducibly from several determinations. This feature is not due to high temperature changes in the morphology of the silica, as no corresponding events were noted in the differential scanning calorimetry traces for the material, and it is known that the first such structural change occurs at

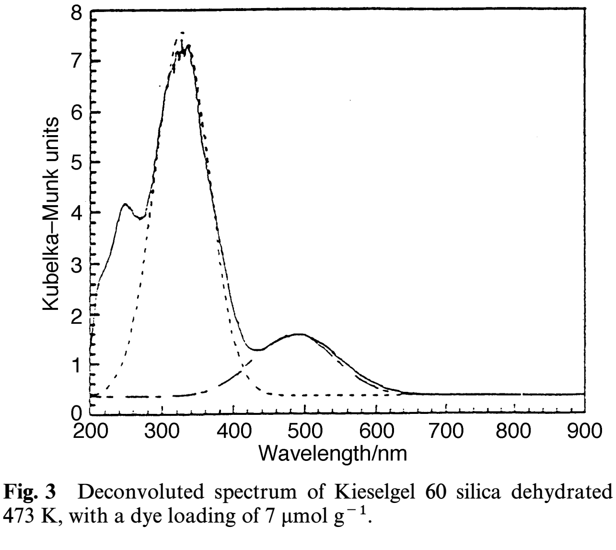

Fig. 3 Deconvoluted spectrum of Kieselgel 60 silica dehydrated at 473 K, with a dye loading of 7 µmol g^{-1}.

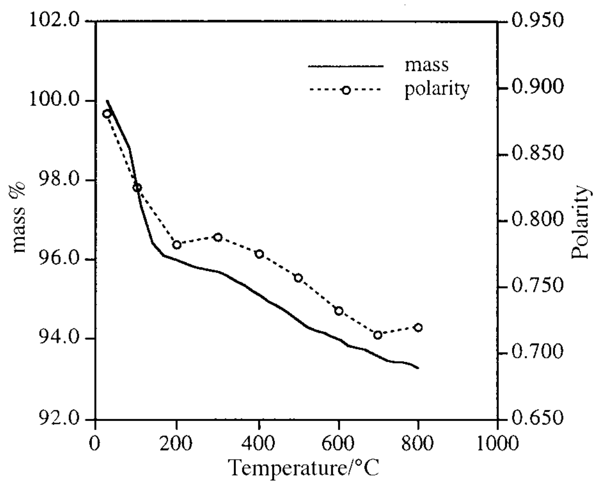

Fig. 4 E_T^N changes as a function of temperature for Kieselgel 60 silica.

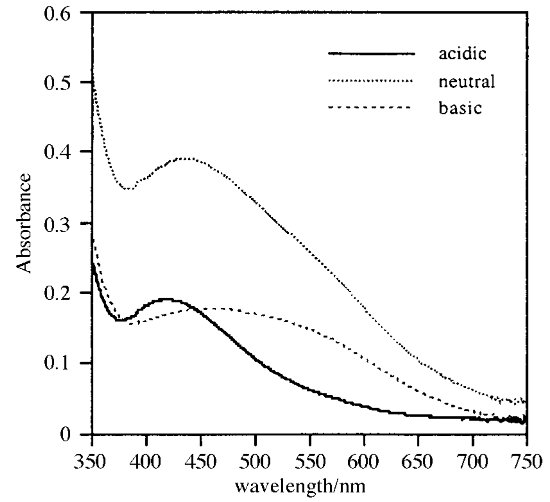

Fig. 5 Spectra of various aluminas: (a) acidic, (b) neutral, (c) basic.

ca. 1058 K.[1] Possible contributors to this feature may include a significant reduction in surface area. Such a change occurs at *ca.* 973–1073 K for such materials, and is related to the condensation of adjacent particles.[1] Other potential sources of this change may include the migration of defects or impurities to the surface.

Aerosil is a fumed silica which has a less hydroxylated surface than the other silicas used. The somewhat lower value obtained for this material is in accordance with this difference.

Micelle templated silicas (MTS) are very high surface area materials (specific surface areas are typically 900–1000 m^2 g^{-1}) and have very narrow pore size distributions. The surface areas are therefore 3–5 times greater than those found for the amorphous silicas. In addition, the hydrophilic/hydrophobic behaviour of the MTS surface[3] significantly differs from other amorphous[25] or crystalline silica surfaces.[26,27] The amounts of water adsorbed on MTSs are close to those adsorbed on hydrophobic pyrogenic silicas at the same water pressure, while the interaction energy is higher than the value measured on the most hydrophilic silica. Moreover, whereas the siloxanes formed upon treatment at high temperature (1073 K) are very resistant towards hydrolysis, the rehydroxylation of similarly treated MTS materials is rapid. This feature has been attributed to the nature of the preparation procedure, where the alkylammonium head groups induce the formation of silanol groups with an unusual spatial distribution and orientation.[3] Values obtained for these materials were significantly lower than for the corresponding silicas, and did not vary particularly with drying temperature. In order to ascertain whether this might be due to the more rapid rehydration of the MTS materials, the experiment was repeated in a glove box using a sealed UV cell. The same results were obtained, and thus probably reflect a more organophilic surface.

3.3 Other inorganic materials

3.3.1 Alumina. The surface of alumina contains basic, amphoteric and acidic sites. Thus the range of surface sites and environments is more varied than with the silicas. The spectra obtained from samples of acidic, neutral and basic aluminas are shown in Fig. 5.

As can be seen, the spectra display significant differences, and in some cases there is a change in band shape, indicating that, for some aluminas at least, it may be possible to distinguish two different surface sites. However, the size of the probe may mean that the observed transition energy is influenced by several adjacent sites, thus delivering an averaged value for regions where a variety of different sites exist together.

Other inorganic materials tested are listed in Table 1. All gave one band for the charge transfer transition, with the exception of zirconia, which may be sufficiently acidic to protonate the dye.

3.4 Organically modified silicas

Several types of modified silicas have been studied using this technique. The traditional method for modifying silicas is the post-treatment or grafting of organosilanes (Fig. 6):

The simple mechanism, shown above, indicates a stepwise condensation of surface silanols and RO–Si units, with the expulsion of ROH. However, several authors have indicated that the simple mechanism does not fit with all the data known. In particular, the work of Blümel[28] and Dubois and Zegarski[29] has hinted at a mechanism which involves surface siloxanes, with chemisorption of ROH taking place to a significant extent.

Given the simple peak shapes measured for unmodified silicas, it would be expected that the results obtained for organomodified silicas would also be average values for the supported organic and the surface. This expectation was met, and simple line shapes were found in all cases, indicating that

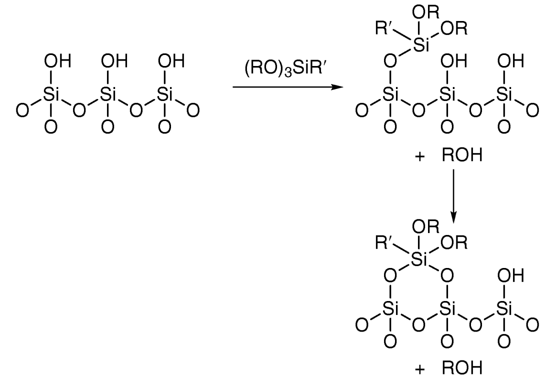

Fig. 6 Postulated grafting mechanism for organofunctionalisation of silicas.

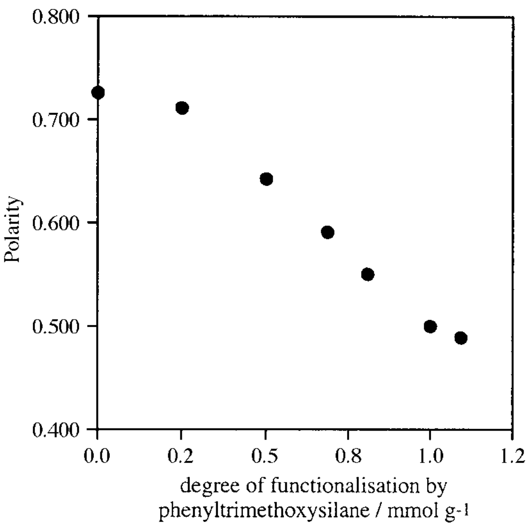

Fig. 7 Polarity as a function of surface coverage for phenyl-functionalised silica.

an average value had been obtained.‡ No evidence of different adsorption sites was found. Results for a variety of functionalised silicas (Kieselgel 100) are given in Table 2.

As can be seen, the functionalisation of silica with a variety of functional groups causes the surface polarity to drop significantly. The influence of the degree of functionalisation was studied by measuring E_T^N values for a series of materials with different loadings. Typical results obtained are given in Fig. 7 for phenyl-substituted silica. Similar results were obtained for aminopropyl, cyanoethyl and trimethylsilyl substituted materials.

As can be seen, there exists a close correlation between surface loading and E_T^N. This allows a rapid and simple estimate of loading to be carried out. The change in absorption energy ΔE_T^N per unit loading can be calculated, and compared to the values obtained for similar liquids. Thus, ΔE_T^N increases in the order cyanoethyl < aminopropyl < imidazole < phenyl < chloropropyl < trimethylsiloxyl. This compares well to the range of E_T^N values found for representative liquids: tetramethylsilane (0.000), benzene (0.111), 1-chlorobutane (0.191), 1-aminobutane (0.213), propionitrile (0.401) and water (1.000). Thus the reduction in polarity measured correlates with the nature of the organic group bound to the surface. As might be expected from a partially covered surface, the E_T^N values found for the modified materials lie between those of the unfunctionalised silica and the functional group introduced. Where silanol population densities are known,[19–23,30] there appears to be a rough correlation with silanol population and transition energy. This is to be expected, since studies of Reichardt's dye in solution indicate that interaction with hydroxylic media cause significant changes in dye transition energy. Thus, the actual value measured for an organically functionalised surface appears to be a function of both silanol density and the nature of the functional group introduced.

3.5 Grafted micelle templated silicas

Grafted MTSs are very high surface area materials (specific surface areas typically 900–1000 m^2 g^{-1}) and very narrow pore size distribution. Surface grafting onto micelle templated silicas has been recently investigated by the group of Brunel.[23,31] Results for dye adsorption experiments on these materials are shown in Table 2.

The polarity of the surface, as measured by Reichardt's dye is very similar to that of silica. IR spectroscopic and microcalorimetric data obtained during water adsorption suggest that the surface of MTS is made up of hydrophobic and hydrophilic patches, and that grafting occurs predominantly on the hydrophobic sites.[26]. This mechanism has recently been confirmed by NMR spectroscopy.[29] The peak shapes obtained upon impregnation of the dye onto silica did not indicate the existence of two such regions. However, it may be possible that dye adsorbed on some regions containing very polar sites (*e.g.* geminal silanols) is protonated, leading to loss

Table 2 E_T^N values for chemically modified silicas

Material	Organic loading/mmol g^{-1}	Pore diameter/nm	A^a/m^2 g^{-1}	Dye loading/μmol m^{-2}	λ_{max}/nm	E_T^N
Silica^b	0	8.5	254	0.04	477	0.967
Silica^b–$OSiMe_3$	0.53	8.3	230	0.04	560	0.630
Silica^b–Ph	1.00	8.4	240	0.05	610	0.500
Silica^b–$(CH_2)_3Cl$	0.64	8.4	250	0.06	554	0.645
Silica^b–$(CH_2)_3NH_2$	0.99	8.2	245	0.03	590	0.546
Silica^b–$(CH_2)_2CN$	0.99	8.4	245	0.04	557	0.636
Silica^b–$(CH_2)_3$N-CH=N–CH=CH	0.97	8.2	240	0.04	611	0.497
MTS^c–$(CH_2)_3Cl$	1.0	2.3	791	0.05	521	0.74^d
MTS^a–$(CH_2)_3Cl$/HMDS^e	1.0	2.1	593	0.06	636	0.45^f
MTS^c–$(CH_2)_3NH_2$	1.9	2.2	809	0.05	520	0.75
MTS^c–$(CH_2)_3NH_2$/HMDS^e	1.9	2.1	625	0.05	593	0.49
HMS^g–$(CH_2)_3NH_2$	1.1	3.6	754	0.03	444	0.90
HMS^g–$(CH_2)_3NH_2$	2.4	3.7	745	0.03	464	0.82
HMS^g–$(CH_2)_3NHMe$	1.0	3.6	695	0.05	446	0.89
HMS^g–$(CH_2)_3NMe_2$	1.1	3.5	715	0.05	449	0.88
HMS^g–$(CH_2)_3Cl$	1.1	3.3	1305	0.025	454	0.86
HMS^g–$(CH_2)_2CN$	1.1	3.7	1039	0.03	452	0.87

[a] Specific surface area. [b] Kieselgel 100 modified with the appropriate silane. [c] Grafted MTS materials. [d] Silanol density 2.1 silanols nm^{-2}; underivatised 2.4 silanols nm^{-2} (ref. 29). [e] Treated with hexamethyldisilazane after grafting. [f] Silanol density 1.5 silanols nm^{-2} (ref. 29). [g] *In situ* preparation.

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‡ Deconvolution of some spectra at low dye loading indicated a small shoulder at the low energy side of the main π–π* transition, between 310 and 330 nm. The origin of this feature is not as yet clear, but may be due to the protonation of the dye by a small number of acidic sites on the surface. Such an effect would lead to loss of the charge transfer band, and the appearance of a π–π* transition from the protonated dye.

of the charge transfer band, or that the polarity of such regions is so high that the charge transfer band is shifted to high energy such that it is under the very intense π–π* band. Microcalorimetric studies of water adsorption on silicas indicate two such regions exist, and show high values of differential adsorption at low coverages.[3]

Although the degree of functionalisation is typically higher than that found for silica, it is likely that the amount of uncovered surface is also much higher. Thus, the polarity might be expected to resemble that of the unfunctionalised material. This is indeed seen (Table 2), polarity dropping only when the surface coverage is very high, or when the surface is treated with hexamethyldisilazane (HMDS), which leads to a high degree of surface coverage by very hydrophobic, non-polar Me_3Si groups. It has been shown that, for these materials, only 30% of silanol groups were end-capped. Nevertheless, surface polarity would be expected to drop significantly even for such an apparently low coverage, as the bulk of the trimethylsilyl group will block access to many of the underivatised silanols.[28,29] Such a trend is in fact seen (Table 2).

3.6 *In situ* prepared organo-HMSs

Macquarrie has recently developed a method for the direct preparation of organically modified hexagonal mesoporous silicas (HMSs).[17] The materials prepared by this route resemble the grafted MTSs in some respects, but differ significantly in others. Principally, the grafting step is replaced by a copolymerisation of tetraethyl orthosilicate and an organo(trimethoxy)silane in the presence of a micellar template. This leads to significant differences in surface chemistry in some respects. For example, the reactivity of *in situ* prepared aminopropyl materials towards imine formation with *e.g.* benzaldehyde is very different, the organo-HMS being much less reactive than the MTS.[34] In terms of surface polarity, these materials all display high $E_{\mathrm{T}}^{\mathrm{N}}$ values, very close to unfunctionalised silica. Only with higher coverage do the $E_{\mathrm{T}}^{\mathrm{N}}$ values begin to drop. This is indicative of a highly polar surface, and a high surface area, meaning that a great deal of the surface is exposed even with loadings of 2.4 mmol g^{-1}. As expected with the much lower surface area silicas (typically 200–300 m^2 g^{-1}, *cf.* the organo-HMSs 750–1400 m^2 g^{-1}) the surface coverage is much greater and the polarity correspondingly lower (Table 2).

3.7 Titration of dye

The experiments described above were carried out by adding the dye solution to the material in question until a visible colour change was observed on the material. This approach is obviously qualitative and the amount of dye required appeared to vary considerably from material to material. This was investigated by measuring the UV–VIS spectrum of samples with varying amounts of dye adsorbed. The major feature noticed was that the amounts required to observe the charge transfer band did indeed vary dramatically depending on the nature of the bound group. Results are summarised in Table 3.

What can be seen is that the underivatised materials require significant amounts of dye before a detectable charge transfer band occurs. Other organically modified materials require differing amounts of dye, with the aminopropyl materials giving definite bands upon addition of only very small amounts of dye. While there remains much to be done in this part of the work, it may be that the materials contain small but significant quantities of sites which are sufficiently acidic to protonate the dye, which is known to remove the charge transfer transition. The presence of amino groups could then neutralise these groups, leading to a much more sensitive system.[1] Such behaviour has been noted with Reichardt's dye before, upon addition of triethylamine to surface-dye complexes, where protonation of the dye was suspected.[12] Thus this 'spectrophotometric titration' method could provide very useful information on the detailed nature of the surface sites in different systems, and is currently being investigated further.

Table 3 Minimum dye quantity (μmol m^{-2}) required to detect the charge transfer band

Silica	0.012
MTS	0.004
chloropropylsilica	0.014
chloropropyl MTS	0.006
Aminopropylsilica	0.85×10^{-3}
aminopropyl MTS	$<0.50 \times 10^{-3}$

Upon continued addition of the dye to the solids, a further change became apparent at high loading. An additional band at 628 nm began to appear, which can be attributed to clusters or microcrystals of the dye resulting from overloading of the surface. For the materials presented thus far, there exists a significant window of loadings where this feature is absent, indicating that the spectral features are due to dye–surface interactions, and not to dye–dye interactions.

3.8 Crosslinked organic polymers

A further extension to the investigations involved the use of insoluble cross-linked organic polymers. Such materials typically have much lower surface areas than the inorganics discussed above, and thus might represent a more difficult challenge. Their surface areas and porosities were measured using nitrogen adsorption, and indicated very low surface area. Their ability to swell in organic solvents makes these results of limited validity. However, their interfacial properties are also of interest, and thus measurement of surface properties is a worthwhile endeavour. Cross-linked polystyrene, cellulose and starch were investigated. It was found to be much more difficult to obtain good spectra for these materials, as loading of the dye was much more difficult, with microcrystals of dye forming even at very low dye : polymer ratios. The microcrystals could be easily characterised by their UV–VIS spectra, which resembled that of the solid dye itself. Despite these difficulties, it did prove possible to obtain useful results from these materials (Table 4).

As can be seen, polystyrene shows an absorption significantly higher than that of most alkylaromatics ($E_{\mathrm{T}}^{\mathrm{N}} = 0.099$ and 0.111 for toluene and benzene respectively). The reason for this behaviour is not clear at present. Cross-linked poly(vinylpyrrolidone) displays a value ($E_{\mathrm{T}}^{\mathrm{N}} = 0.371$) which is typical of amides. Cellulose ($E_{\mathrm{T}}^{\mathrm{N}} = 0.51$) and starch ($E_{\mathrm{T}}^{\mathrm{N}} = 0.57$) both resemble medium chain (C_4–C_6) alcohols ($E_{\mathrm{T}}^{\mathrm{N}} =$

Table 4 Values of λ_{max} and $E_{\mathrm{T}}^{\mathrm{N}}$ for Organic polymers[a]

Polymer	λ_{max}/nm	$E_{\mathrm{T}}^{\mathrm{N}}$
Polystyrene[b]	752	0.225
Amberlite XE305[b]	729	0.278
Amberlite XAD4[b]	752	0.225
Cellulose[c]	582	0.570
Starch[d]	610	0.517
Poly(vinylpyrrolidone)[e]	669	0.371

[a] Owing to the swelling behaviour of the different polymers, the specific surface areas (as measured by nitrogen adsorption) may not reflect the surface area accessible to the dye molecule in the adsorption experiment. Thus, the dye loadings have not been given. In all cases loadings of the dye were <1 μmol g^{-1}). [b] Crosslinked with divinyl benzene. [c] ex Aldrich. [d] ex Aldrich. [e] ex Aldrich, crosslinker unknown.

0.50–0.60), again fitting in well with what might be expected for polyhydroxylated organic polymers, but, interestingly in light of their polyhydroxylated structures, significantly less polar than most diols (0.65–0.73). Thus, the technique can be used readily for insoluble organic polymers, even though their surface areas are much lower (typically a few $m^2\ g^{-1}$) than those of the inorganics discussed above.

4 Conclusions

Reichardt's dye can be adsorbed onto a range of insoluble materials. Measurement of the charge transfer transition of the dye allows estimates of the surface properties to be carried out in a quick and simple manner. Values obtained correlate well with the known composition of the surface of the materials; in most cases these values are best considered as an average of all the surface species. As with solution studies of this dye, the interaction of the dye with hydroxylic functions appears to be one of the dominant interactions in determining the adsorption maximum.

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