

Surface energy and surface area measurements by ^{19}F MAS NMR of adsorbed trifluoroacetic acid

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Trifluoroacetic acid, when adsorbed on the surface of inorganic materials, is a useful ^{19}F NMR probe molecule for studying surface properties including surface energy and surface area.

Knowledge of the properties of surfaces is extremely valuable in heterogeneous catalysis and other disciplines, and may help in predicting reaction rates and mechanisms, as well as understanding diffusion and poisoning effects. However, it is often difficult to characterise irregular or amorphous catalyst surfaces. Specific surface area and porosity information may be gained from N_2 absorption measurements but, like solvents, surfaces may become involved in many specific and non-specific interactions that are not revealed by these methods. A number of probe-based methods have been reported, in which a surface is studied indirectly by measurement of some property of an adsorbed molecule, such as the position of IR or NMR peaks.^{1,2} ^{19}F -MAS NMR seems particularly promising—it is sensitive and rapid with an extremely wide chemical shift range (approaching 1000 ppm) and spectra can typically be obtained in less than two minutes. A ^{19}F -NMR approach has been used by Fry *et al.* to quantify hydroxyl groups on silica gel and fibres by reaction with a trifluoromethyl-containing silane, a method which was able to discriminate between surface and in-pore sites.³ Changes in ^{19}F and ^{13}C NMR spectra have also been reported when benzenoid compounds are adsorbed on surfaces using a solid–solid ball-milling technique.⁴

We have been investigating small fluorine-containing molecules as probes for obtaining information about catalyst surfaces *via* solid state NMR. Trifluoroacetic acid (TFA) has emerged as a leading candidate as it has a suitable boiling point and volatility, and a high fluorine content which allows detection even at very low surface concentrations. The position of the chemical shift of TFA (δ_{obs}) when adsorbed on solid surfaces has been found to be extremely sensitive, not only to the nature of the surface but also to the surface concentration of the probe itself, and this has proved extremely useful as a procedure for characterising surfaces. Several materials commonly used in catalysis were selected for study: a trimethylsilanised silica, two silicas, two aluminas, titania and three carbon-type materials.^{5,6}

A range of samples were prepared containing the material under investigation mixed with varying amounts of TFA, and ^{19}F MAS NMR spectra were obtained for each of these under identical conditions.⁷ The position of the maximum intensity peak in the NMR spectra (δ_{obs}) has been used for the characterisation of the samples. Running similar samples three times, and the same sample on separate days confirmed the reproducibility of these measurements.

Plotting δ_{obs} against surface concentration⁸ reveals that, whereas at low concentrations δ_{obs} is characteristic for the surface studied, at high concentrations ($\geq 5 \mu\text{mol m}^{-2}$) δ_{obs} becomes equal for each material. NMR peaks became sharper in this high concentration domain and we can propose that TFA assumes liquid-like behaviour ($\delta_{\text{obs}} = \delta_{\text{liq}}$). In this case it is possible (and sensible) to express the chemical shift as $\Delta\delta$, where $\Delta\delta = \delta_{\text{obs}} - \delta_{\text{liq}}$. The values at lowest concentration of TFA ($\Delta\delta_{\text{max}}$) are shown in Table 1 along with other physical data for these materials. Trimethylsilanised silica gel appears at one end of the scale ($\Delta\delta_{\text{max}} = -1.0$ ppm) and two of the carbon materials occupy the other extremity ($\Delta\delta_{\text{max}} = 7.0, 8.0$ ppm). These carbons both have very low oxygen

contents (measure by XPS and elemental analysis) and are essentially non-hydroxylic. The two unfunctionalised silica gels have surfaces rich in hydroxyl groups and fall between these extremities, indicating that $\Delta\delta_{\text{max}}$ is not simply a measure of protonation or hydrogen bonding. (A third carbon material with a $\Delta\delta_{\text{max}}$ comparable to the silicas contained a much higher oxygen content and presumably also has a hydroxylic surface). Despite the acidic nature of the TFA probe, no significant difference between basic and neutral aluminas was observed.

Because surface area and surface concentration are known, it is possible to calculate the mean distance between the probe molecules (D). When $\Delta\delta$ is plotted against D , three distinct domains are apparent:

(i) A region of isolated molecules (low concentration region) in which the chemical shift ($\Delta\delta_{\text{max}}$) remains unchanged with distance and is characteristic for each surface studied;

(ii) A region in which the chemical shift changes rapidly with distance. The probe molecules can now 'feel' one another, and this effect increases with decreasing D ;

(iii) A high concentration region in which the chemical shift remains unchanged with distance. This is a liquid-like or condensed domain; further increase in concentration (*i.e.* decrease in D) produces no significant change in chemical shift. The chemical shift for the region is similar for all surfaces studied so far. In fact, the molecules cannot actually get nearer than close-packing, but are now forming 3-dimensional clusters.

We have found that boundaries between these regions for all surfaces occur at the same intermolecular distances. Furthermore if the plots are normalised by dividing by $\Delta\delta_{\text{max}}$ for each material ($\Delta\delta^{\text{N}} = \Delta\delta/\Delta\delta_{\text{max}}$) it becomes apparent that all points for all samples lie on a single line (Fig. 1).

The chemical shift of a single adsorbed molecule may be expressed as a number of terms that represent contributions from the various types of interaction to which it is subjected.³ These include the intrinsic nature of the probe molecule (δ_{TFA}), the proximity of neighbouring adsorbed molecules ($\delta_{\text{neighbours}}$), and the nature of the surface. The surface itself may involve complex contributions from both specific chemical effects (*e.g.* hydrogen bonding or electron pair interactions, δ_{chem}), and from physical properties, *i.e.* electric (δ_{E}) and magnetic (δ_{M}) fields. For a single molecule:

$$\delta_{\text{obs}} = \delta_{\text{TFA}} + \delta_{\text{neighbours}} + \delta_{\text{chem}} + \delta_{\text{E}} + \delta_{\text{M}}$$

Table 1 BET surface area (S_{BET}), change in ^{19}F NMR chemical shift ($\Delta\delta$), Dubinin–Radushkevitch energies (E_{DR}) and Reichardt's E_{T}^{N} measurements for materials studied¹⁰

Material	$S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$	$\Delta\delta_{\text{max}}$	$E_{\text{DR}}/\text{kJ mol}^{-1}$	E_{T}^{N}
Silica–OSiMe ₃	263	−0.99	11.8	0.63
TiO ₂	47.4	0.77	12.3	0.77
Silica 1	315	1.45	14.5	0.97
Silica 2	457	1.75	14.3	0.88
Carbon 3	1045	2.11	15.8	—
Alumina1 (basic)	173	3.40	14.4	0.93
Alumina2 (neutral)	157	3.47	14.9	1.07
Carbon2	523	7.02	21.7	—
Carbon1	867	8.01	21.3	—

At the limits, where D approaches infinity, or the intermolecular distance in the liquid, two different equations may be written:

$$D \rightarrow \infty; \delta_{\text{obs}} = \delta_{\text{TFA}} + \delta_{\text{chem}} + \delta_{\text{E}} + \delta_{\text{M}} = \delta_{\text{surface}}$$

$$D \rightarrow D_0; \delta_{\text{obs}} = \delta_{\text{TFA}} + \delta_{\text{neighbours}} = \delta_{\text{liquid}}$$

These equations describe the behaviour in regions (i) and (iii). In between these limits, all experimental points fit the equation: $\Delta\delta^{\text{N}} = a + b \cdot D^x$ ($a = 0.99 \pm 0.02$; $b = -55.1 \pm 3.4$; $x = -2.95 \pm 0.04$, determined by non-linear regression) This D^{-3} dependence may be due to nuclear shielding by the electric field of neighbouring molecules; the interaction energy between a pair of fixed dipoles also shows a D^{-3} dependence.⁹ The distance at which this equation is no longer valid (D_0) should correspond to the average distance between TFA molecules in the liquid phase. D_0 was found experimentally by this method to be 3.8 Å, which compares well with the dimensions of TFA: calculation from liquid density gave an average diameter of 5.0 Å; computer-modelling of TFA in Hyperchem gave a value for the smallest dimension of 4.1 Å, very close to our value.

In order to validate our methodology further, we have compared our findings with existing measures of surface properties. Fig. 2 shows plots of $\Delta\delta$ against the normalised energy of the π - π^* transition (E_{T}^{N}) for Reichardt's dye,¹⁰ which we have found to be a useful estimate of surface polarity,² and also against the Dubinin–

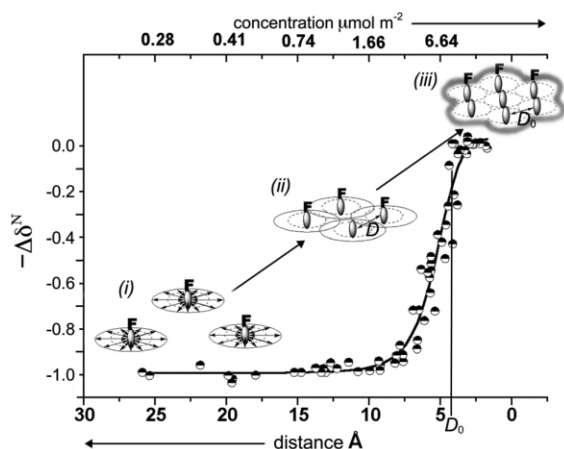


Fig. 1 Plot of variation in $\Delta\delta^{\text{N}}$ with mean inter-molecular distance for all materials. F represents a fluorinated probe molecule.

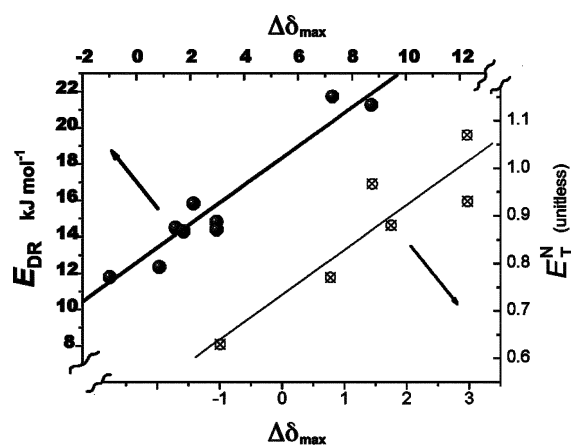


Fig. 2 Correlation of $\Delta\delta_{\text{max}}$ with E_{T}^{N} and E_{DR} measurements

Radushkevitch measure of surface energy (E_{DR}), which is calculated from N_2 adsorption methods.¹¹ The high E_{DR} values for the carbons 1 and 2 are particularly revealing: unlike the silicas these surfaces are not hydroxylic and we may not have expected them to show such a high $\Delta\delta$. They do, however, contain regions of electron-rich graphite-like structure which must contribute greatly to surface energy, and the correlation between high E_{DR} and large $\Delta\delta_{\text{max}}$ confirms that the change in chemical shift is largely due to physical and not specific chemical interactions: $\delta_{\text{surface}} \approx \delta_{\text{E}} + \delta_{\text{M}}$.

In summary, by adsorbing TFA on irregular surfaces we obtain a characteristic chemical shift ($\Delta\delta$) for the surface which correlates well with E_{DR} surface energy as obtained from N_2 adsorption measurements, and with E_{T}^{N} polarity values. The $\Delta\delta_{\text{max}}$ parameter shows no correlation with either the total pore volume or the volume of micropores.

In these experiments we have used materials with known surface areas, but, because a distinct change in behaviour is seen at the point where the whole surface is saturated with probe molecules, it is clearly possible to use this approach to measure a specific surface area for an unknown surface. Surface area is more usually measured by N_2 adsorption, but 'real-life' catalysis involves the use of larger molecules which may not be able to access the entire surface (e.g. micropores) seen by adsorbed N_2 . However, by extension of our method it should also be possible to measure a surface area specific to any desired molecule, simply by adsorbing a fluorinated analogue of that molecule and observing the behaviour of its ^{19}F NMR chemical shift.

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Notes and reference

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- 7 Mixtures of 1 g of material with 2 g TFA down to 4 g of material with 0.05 g TFA were investigated. The mixtures were not filtered or dried. Spectra were obtained on a Bruker Avance 400 spectrometer in a 4 mm zirconia rotor spinning at 12 kHz. A single-nucleus, one pulse (ZG) acquisition method was used, and 16 scans collected for each sample.
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