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Quantitative determination of surface species and adsorption sites using Infrared spectroscopy

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ABSTRACT

An overview of the application of FTIR to the quantification of adsorption sites on solid acids, metal particles and to hydrocarbon chains formed during Fischer Tropsch synthesis is reported. The procedures employed in obtaining molar absorption coefficients for transmittance FTIR are described along with a review of pertinent data reported for the three topic areas covered. The limitations and challenges in each case are outlined.

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1. Introduction

Infrared spectroscopy is possibly one of the most widely used tools in the characterisation of heterogeneous catalysts [1]. Amongst the most widely used applications, there are numerous examples of its use in obtaining qualitative information regarding; bulk phase vibrations in solids such as oxides, hydroxides, carbides, carbonates and other phases, surface terminating groups such as hydroxyls [2], bulk and surface species such as carbonates, acetates and acrylates [3], nitrates [4] and sulfates [5] which undergo transformation during a catalytic cycle, the use of probes such as ammonia and pyridine to determine acidic groups on oxide surfaces [6,7], the use of CO, NO to study sites on supported metals, oxides [8] and sulphides. However, the use of photons means that the technique is not limited in terms of the pressure and temperature of the reaction environment and the fact that the technique is non-invasive and non-destructive means that it may be coupled with other analytical procedures. These significant advantages over many other techniques provide opportunities to conduct experiments which might provide crucial answers to many key questions in catalysis such as, what are the active sites, how many of these exist (under operating conditions) and what are the nature of the reactive intermediates? Unfortunately, use of the technique is not without its limitations and challenges and these are mainly related to the slow scan speeds with respect to the residence time of intermediates, the spectra may be dominated by non-reactive "spectator species" which need to be discriminated from the active species, and the general difficulties associated with quantification. In this study, a review of some of the attempts to meet these challenges is described, with particular focus on quantification, using examples of acid sites on oxides, sites on supported metals and bimetallics, and hydrocarbon chain growth during Fischer Tropsch (FT) synthesis.

2. Measurement of absorption coefficients

To make quantitative measurements and interpretations from infrared spectra, the molar absorption coefficient(s) of the probe molecule must be known or established. Molar absorption coefficients can be determined assuming that the system (absorbent and substrate) conforms to Beer-Lambert type behaviour. The application of values taken from e.g. collection of solid phase or liquid phase of the pure materials may give rise to significant error given that (lateral) interactions in these phases

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may be absent for the molecule or ion in an adsorbed state. To determine the absorption coefficient for a particular mode, measurement of both the integrated band area and the number of moles adsorbed in that particular mode are required. Previous studies have measured number of moles adsorbed simultaneously with recording the spectrum *in situ*, either through volumetric gas dosing into an infrared cell [9,10] or *via* gravimetric measurements using a microbalance [7]. Reduction of errors can be achieved by the simultaneous measurement of both uptake and FTIR spectrum using specially designed cells [11] and often abbreviated as AGIR (combined IR and gravimetric analysis) [12]. Although the use of DRIFTS to provide quantitative analysis has been reported [13,14], and this approach may overcome some of the challenges in preparing homogenous, uniform thickness self-supporting discs [15] for transmission spectroscopy, the need to determine an additional unknown term to deal with the scattering coefficient provides a different set of challenges. For the sake of brevity and coherence in this report, we shall limit description to the use of data obtained by transmission FTIR.

3. Application to solid acids

Acid sites present on the surface of catalytic materials and support arise due to the exposure of cationic metal centres (Lewis acid) or hydroxyl groups (Brønsted acid) with their strength determining the catalytic activity and often selectivity of the parent metal oxide, mixed oxide or zeolite. A difference in ionic radius between the metal cation and oxygen in single oxides leads to the formation of both types of acid site, with dissociative adsorption of water producing hydroxyl groups. In mixed oxides, distinct valencies of the metals create oxygen vacancies or hydroxyl groups through charge balance at the surface whereas in zeolites the sites are generally found within the pores of the material [16]. Solid acid catalysis implements the principles of Green Chemistry and is used widely in the petrochemicals industry for acylation, alkylation, amination, cracking, hydroxyalkylation and isomerisation reactions. Product selectivity is altered by controlling the strength and number of Lewis/Brønsted acid sites and the surface area/porosity during synthesis or pre-treatment, with an understanding of the surface under reaction conditions, particularly the dispersion of active sites, of paramount importance [17].

The application of basic probe molecules to study oxide surfaces as-prepared, pretreated or under catalytic conditions is widespread in the literature and includes probes such as alcohols, aldehydes, ammonia, alkyl-amines, imines, ketones, nitriles, pyridine, alkylpyridines, thiols and water with the molecular perturbation arising from adsorption typically determined by FTIR spectroscopy [1]. While these perturbations of the different vibrational modes gives a qualitative indication of the presence of one or more type of adsorption site, the relative intensity (or integrated intensity) of the absorption band is not an indicator of the relative abundance of such sites. In order to quantify the number of acid sites and hydroxyl groups on an oxide surface or within the pore channels of zeolites, it is necessary to determine an absorption coefficient to relate the signal intensity of the probe molecule in the FTIR spectrum with the number of adsorption sites in the sample (equation 1).

$$n_T = \frac{AC_d}{\varepsilon m} \tag{1}$$

where n_T is the number of adsorbed species (μmol g^{-1}), A is the integrated absorbance of a particular mode (cm^{-1}), C_d is the area of the IR disc (cm^2), ε is the absorption coefficient (cm μmol^{-1}) and m is the mass (g) of the sample/adsorbent.

$$n_T = \frac{A_1 C_d}{\varepsilon_1 m} + \frac{A_2 C_d}{\varepsilon_2 m} \tag{2}$$

It may be seen from the expression (equation 1) that the absorption coefficient may only be extracted if, in addition to the integrated intensity of the absorption band due to adsorption on a particular site, the number of adsorbed species is determined and this may involve simultaneous or separate measurement of adsorbate uptake by gravimetric or volumetric means. Clearly the greater the number of adsorption modes/types of sites, the greater the number of absorption coefficients that must be determined (equation 2) and to equate these to the total number of adsorbed species (which is a sum with no distinction of the different species), a number of terms must be generated and coefficients extracted by simultaneous equations where the number of equations equals the number of unknowns. A series of values of A and of n_T may be generated by varying the coverage through controlling dosage/exposure or by measuring at different temperatures. Clearly, it must be assumed that the absorption coefficients are not influenced by coverage and this tends to be the case on an oxide surface where the adsorbates are sufficiently far apart as to avoid intermolecular interactions.

The following section provides examples of cases where this approach has been made to provide quantitative analysis of adsorption sites on solid acid surfaces through the adsorption of basic probe molecules and thus subscripts 1 and 2 in equation 2 refer to adsorbate on Lewis and Brønsted sites.

To modify the acidity of solid oxides, dopants are commonly used, with sulfate being the most widespread, particularly in the case of zirconia. In this case, acid properties are determined by calcination temperature of the zirconia precursor, sulfate concentration and *in-situ* thermal activation. Pyridine adsorption is recognised as a technique to study solid acidity as Lewis and Brønsted sites can be distinguished by their distinct absorption bands at 1450 cm^{-1} and 1540 cm^{-1}, respectively. To study the effect of sulfate loading and sulfation procedure on the surface acid densities of a series of silica-zirconia aerogels, combined TG/FTIR techniques were employed during pyridine adsorption. Absorption coefficients were determined as 1.00–2.08 cm μmol^{-1} at 1450 cm^{-1} for Lewis-bound pyridine and 0.64–1.66 cm μmol^{-1} at 1540 cm^{-1} for pyridinium (Table 1). Non-sulfated samples gave values of 1.78 cm μmol^{-1} at 1450 cm^{-1} and 0.53 cm μmol^{-1} at 1540 cm^{-1}. It was found that *ex-situ* addition of sulfate greatly reduced the Brønsted acid site density whereas Lewis acidity increased in terms of density but not strength. Brønsted site coverage in the silica-zirconia regions, by the dissolution and re-precipitation of amorphous Lewis-acid forming zirconia during acid treatment was attributed as the cause [18].

Further work demonstrated that changes in preparation methods and zirconia concentrations had little effect on absorption coefficient values (1.53–1.59 cm μmol^{-1} at 1450 cm^{-1} and 1.21–1.27 cm μmol^{-1} at 1540 cm^{-1}) whereas sulfation led to extensive variation (1.00–2.08 cm μmol^{-1} at 1450 cm^{-1} and 0.64–1.66 cm μmol^{-1} at 1540 cm^{-1}) (Table 1) [19]. It was suggested that hydroxylated surface sulfate species brought pyridinium ions into sufficiently close proximity that they electronically interacted, lowered the absorption coefficient and in turn called into question the use of one absorption coefficient for samples covering a range of sulfate loadings. The most widely cited values in the literature at the time were those determined by Emeis [20] (2.22 cm μmol^{-1} at 1455 cm^{-1} and 1.67 cm μmol^{-1} at 1545 cm^{-1}) and it was argued that these were less applicable as they sat towards the high end of the range in the literature, with the new values lying central in the range. By combining the perturbation of molar absorption coefficients of both types of adsorbed pyridine and *ab initio* calculations for sulfate structures, the development of acid site density as a function of sulfate loading was recognised [21]. This may be related also to the concern that this approach overestimates the concentration of Lewis

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