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Quantitative Analysis of Adsorbate Concentrations by Diffuse Reflectance FT-IR

Jinda Sirita,^{†,‡} Sukon Phanichphant,[‡] and Frederic C. Meunier^{*,†}

CentACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, Northern Ireland, United Kingdom, and Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

Fully quantitative analyses of DRIFTS data are required when the surface concentrations and the specific rate constants of reaction (or desorption) of adsorbates are needed to validate microkinetic models. The relationship between the surface coverage of adsorbates and various functions derived from the signal collected by DRIFTS is discussed here. The Kubelka–Munk and pseudoabsorbance (noted here as absorbance, for the sake of brevity) transformations were considered, since those are the most commonly used functions when data collected by DRIFTS are reported. Theoretical calculations and experimental evidence based on the study of CO adsorption on Pt/SiO₂ and formate species adsorbed on Pt/CeO₂ showed that the absorbance (i.e., = log 1/R', with R' = relative reflectance) is the most appropriate, yet imperfect, function to give a linear representation of the adsorbate surface concentration in the examples treated here, for which the relative reflectance R' is typically > 60%. When the adsorbates lead to a strong signal absorption (e.g., R' < 60%), the Kubelka–Munk function is actually more appropriate. The absorbance allows a simple correction of baseline drifts, which often occur during time-resolved data collection over catalytic materials. Baseline corrections are markedly more complex in the case of the other mathematical transforms, including the function proposed by Matyshak and Krylov (*Catal. Today* 1995, 25, 1–87), which has been proposed as an appropriate representation of surface concentrations in DRIFTS spectroscopy.

The investigation of chemical reactions by in situ and operando diffuse reflectance FT-IR (DRIFTS) spectroscopy can bring many invaluable insights into the mechanism of heterogeneous catalytic reactions.^{1–6} Recent work by our laboratory has re-emphasized

that chemical steady-state conditions must be maintained to investigate the true reactivity of surface species under reaction conditions,^{2,7–9} stressing the advantage of using chemical-steady-state isotopic transient techniques to investigate the true reactivity of adsorbates. A DRIFTS reactor is particularly suited to this type of spectrokinetic investigation since the catalyst powder can be used directly as such, whereas transmission techniques require pressing wafers, which can lead to mass-transport limitations and catalyst modifications. DRIFTS spectroscopy possesses a number of other advantages over transmission FTIR and is becoming the most widespread FTIR technique for catalytic applications at the gas–solid interface. DRIFTS exhibits a higher sensitivity with respect to surface species and strongly absorbing samples such as carbon-based materials can be studied.^{10–18} This increased popularity is also due to the availability of a number of affordable commercial cells,¹⁹ while a few research groups have built custom-made cells.^{20,21}

The qualitative analysis of the DRIFTS spectra is sufficient to assess the nature of the adsorbates present. However, a fully quantitative analysis of DRIFTS data is required when the surface concentrations and the specific rate constants of reaction (or desorption) of adsorbates are needed to carry out complete spectrokinetic studies. Ideally, a function of the DRIFTS intensity that is linear with the adsorbate surface concentration would be preferred. Griffiths et al.^{10,12,13} and several other groups^{15,22–25} have

* Author to whom correspondence should be addressed. E-mail: f.meunier@qub.ac.uk

[†] Queen's University Belfast.

[‡] Chiang Mai University.

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discussed the quantification of DRIFTS analyses and observed that the domains of linear response between solute/sorbate concentration and DRIFTS intensity transform were somewhat narrow.

It is surprising that the nature of the DRIFTS intensity function to be used to represent the surface concentration of adsorbates seems yet rather unclear. A brief survey of the numerous papers dealing with DRIFTS studies of adsorbates published (particularly in heterogeneous catalysis journals) over the 2005–2006 period reveals that the Kubelka–Munk function was used in about half of the papers, while the absorbance ($= \log 1/R$) function was used in the other half. The basis of the choice of function was usually not discussed. The lack of clarity as to which intensity transform to use is partly due to the fact that there is no direct means of measuring the surface concentration of an adsorbate and the corresponding DRIFTS signal intensity. Note that this is no longer the case for transmission FTIR, for which a combined gravimetric microbalance-IR cell has been built.^{26,27}

The first part of this paper briefly discusses the basis of DRIFTS quantitative analysis for both “solute in a solid” and “adsorbate on a solid” systems, the latter case being the one most relevant to heterogeneous catalysis. Both theoretical and experimental considerations are presented to assess the most appropriate mathematic transformation to be used to relate adsorbate surface concentration and DRIFTS signal. The experimental data are based in part on the adsorption of CO on Pt/SiO₂. Some absorbance spectra already reported elsewhere²⁸ related to the reactivity of formate species over Pt/CeO₂ have been reused to allow comparison of those with other intensity transformations.

THEORY

The basis of the diffuse reflectance theory used to quantify the concentration of a solid solute in a nonabsorbing matrix was developed by Kubelka and Munk^{29,30} and widely applied to the mid-IR regions^{10,22,23} and sometimes to the UV–vis³¹ and near-IR¹³ regions. The Kubelka–Munk formula (eq 1) relates the absolute reflectance R_∞ of the scattered radiation ($R_\infty =$ intensity scattered divided by that of the incident radiation) to the sample absorption and scattering coefficients k and s , respectively.

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{k}{s} \quad (1)$$

The equation refers to a semiinfinite thick sample, a condition that is achieved in practice with catalyst beds thicker than a couple of millimeters for typical catalytic materials.³² The incident intensity is usually not known and difficult to measure. Therefore,

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a typical DRIFTS experiment usually consists, first, in measuring the diffusively reflected intensity $I_\infty(\text{ref})$ over a reference sample (poorly absorbing and highly scattering medium such as finely divided KBr particles for the mid-IR¹⁰) and, second, measuring the intensity $I_\infty(\text{sample})$ over the sample of interest. However, the moisture level of reference salts and the particle size of those will have an effect on the medium absorptivity and scattering properties,¹⁰ respectively. Therefore, experiments carried out using a 180° configuration (such as that of the Spectra-Tech Collector used here) usually rely on using a flat perfectly reflecting metallic mirror as reference, which allows measuring with a good precision the incident intensity (otherwise largely underestimated when using KBr with commercial cells, which do not comprise a full integration sphere). The value of the ratio $I_\infty(\text{sample})/I_\infty(\text{ref})$ is then taken as an approximate value for R_∞ . For a solute of absorptivity $k = 2.303\epsilon C$, where ϵ is the molar absorptivity and C the solute concentration in a nonabsorbing matrix, the Kubelka–Munk function $f(R_\infty)$ is directly proportional to C :

$$C = \text{constant} \times f(R_\infty) \quad (2)$$

In practice, many of the conditions required for the Kubelka–Munk theory to apply are not often met, e.g., because of the presence of Fresnel (i.e., specular, mirror-like) reflection, matrix absorption, and nonuniform optical properties of the sample.²² Signal corrections can be made, even for nondiluted samples, but the data treatment is complex and the effect of the sample micro- or nanostructure will also affect the scattering coefficient, making the comparison difficult between differently prepared samples.²² In many cases, simple calibration curves have shown that the Kubelka–Munk equation is not linear with respect to the concentration of the solute, displaying a curved¹³ or broken-line shape.²³ Olinger and Griffiths¹³ have proposed that in the case of strongly absorbing matrices, such as that of most catalytic materials, the best linear representation of a solute concentration is given by $\log(1/R)$, noted “absorbance” by analogy with the absorbance $= \log 1/T$ measured in transmission IR:

$$C = \text{constant} \times \log \frac{1}{R_\infty} \quad (3)$$

Matyshak and Krylov³³ have stressed that the quantification of *adsorbates* (as opposed to solutes) in DRIFTS measurements should actually be derived from a modified Kubelka–Munk function. Starting from eq 1, these authors simply added a term due to the absorbance of a surface species of surface concentration θ and absorptivity ϵ' when considering the reflectance R measured in the presence of the adsorbate:

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k + \epsilon'\theta}{s} \quad (4)$$

By combining eq 1 and eq 4, it can be shown that the surface concentration θ is proportional to a simple function of R_∞ and R ,³³

(33) Matyshak, V. A.; Krylov, O. V. *Catal. Today* **1995**, *25*, 1–87.

which we name Matyshak–Krylov function $MK(R, R_\infty)$ for the sake of convenience:

$$MK(R, R_\infty) = \frac{(R_\infty - R)}{R_\infty} \left(\frac{1}{R} - R_\infty \right) \quad (5.1)$$

$$\theta = \text{constant} \times MK(R, R_\infty) \quad (5.2)$$

where R_∞ and R are the catalyst reflectance and the (catalyst + adsorbate) reflectance relative to the reference sample, respectively. It is worth mentioning that the Matyshak–Krylov function shown above is not, to our knowledge, available in any spectrometer software. Therefore, either the Kubelka–Munk or the absorbance ($= \log 1/R$) functions are typically used to represent surface species concentrations, although neither of those may be a perfect representation of surface concentration, as shown in the following sections.

EXPERIMENTAL SECTION

The DRIFTS cell (high-temperature environmental cell with Collector assembly from Spectra-Tech) was located in a Bruker Equinox 55 spectrometer, operating at a resolution of 4 cm^{-1} , and 256 scans were typically collected at a scanner velocity of 20 kHz, using a MCT detector. The CO and Ar used here were supplied by BOC (purity higher than 99.95%). The gas flows were controlled by Aera mass flow controllers, which were regularly calibrated. The silica support used was DAVICAT-1373 from Davidson Catalysts. Platinum was deposited on the silica by incipient wetness impregnation, using a solution of platinum nitrate (15.8% assay, Alfa Aesar). The sample was then heated at $90 \text{ }^\circ\text{C}$ under a slight vacuum for 2 h and subsequently calcined in air in a muffle furnace using a ramp rate of $2 \text{ }^\circ\text{C}/\text{min}$ up to $400 \text{ }^\circ\text{C}$ and held at this temperature for 2 h. The catalyst exhibited a surface area of $190 \text{ m}^2 \text{ g}^{-1}$, the platinum content was 2 wt%, and the Pt dispersion was 22%. The bare silica support was treated in a similar manner as that of the Pt-based catalyst to ensure that the state of the silica was identical for both materials during the DRIFTS analysis. The mechanical mixtures made of different proportions of SiO_2 and of 2% Pt/ SiO_2 were reduced in situ in the DRIFTS cell in 30% H_2 in Ar at $250 \text{ }^\circ\text{C}$ for 15 min prior to CO adsorption at room temperature. A gas stream of 1% CO in Ar was passed over the sample during the collection of the DRIFTS data. The 2% Pt/ CeO_2 catalyst was provided by Johnson Matthey and exhibited a specific surface area of $180 \text{ m}^2 \text{ g}^{-1}$. The Pt dispersion was 17%. The details of the reverse water–gas shift and desorption experiments are reported elsewhere.²⁸

RESULTS AND DISCUSSION

Definition of the Intensities Involved. Three types of single scans are typically recorded during a spectrokinetic experiment carried out in the diffuse reflectance mode. Such scans are reported in Figure 1, which gives the details of the 2150–2050 cm^{-1} region, in which the carbonyls adsorbed on Pt usually display a strong absorption band.

First, a reference spectrum should be recorded to determine the initial intensity I_0 , by using a nonabsorbing sample or most commonly a mirror. The I_0 single scan reported in Figure 1 was obtained by using an Al mirror in place of the sample. Second,

MCT detector signal /a.u.

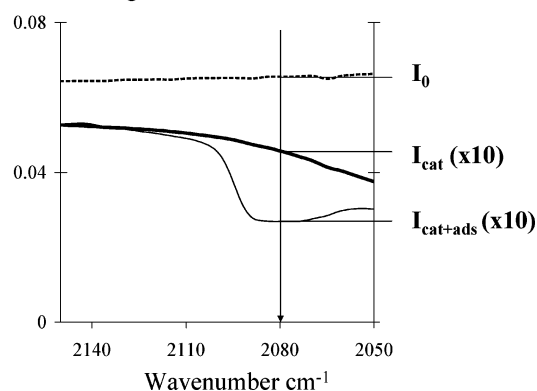


Figure 1. Single scan DRIFTS spectra recorded over a mirror (dashed line) and a Pt/ SiO_2 catalyst at $20 \text{ }^\circ\text{C}$ (solid lines). The spectrum before exposure to $\text{CO}(\text{g})$ (thick solid line) and that under 1% $\text{CO}(\text{g})$ in Ar (thin solid line) are shown. The corresponding intensities at 2080 cm^{-1} are highlighted.

the signal I_{cat} of the catalyst free of adsorbates (e.g., after a pretreatment in an inert gases or under vacuum) is collected. The intensity I_{cat} is typically 1 order of magnitude lower than that of I_0 , as shown in Figure 1 for the case of our Pt/ SiO_2 . As mentioned in the Theory section, R_∞ is defined by:

$$R_\infty = I_{\text{cat}}/I_0 \quad (6)$$

Third, the signal $I_{\text{cat+ads}}$ is measured over the catalyst in the presence of the adsorbate. The band associated with the presence of Pt-bound carbonyl is clearly observed in Figure 1, as the Pt/ SiO_2 catalyst was exposed to 1% CO at room temperature. As described in the Theory section, the sample reflectance is defined by:

$$R = I_{\text{cat+ads}}/I_0 \quad (7)$$

and the relative reflectance R' , which is the measure usually obtained when no mirror spectrum is collected, is given by:

$$R' = I_{\text{cat+ads}}/I_{\text{cat}} \quad (8.1)$$

$$R' = R/R_\infty \quad (8.2)$$

In the case of CO adsorbed on Pt/ SiO_2 at $20 \text{ }^\circ\text{C}$ given in Figure 1, the relative reflectance R' was ca. $0.6 = 60\%$, representing the value of R' at full coverage of Pt by CO (Note: lower than full coverage under CO is only obtained above $300 \text{ }^\circ\text{C}$ over this type of sample³⁴).

Mathematical Transform of the DRIFTS Signal: Modeling.

The intensity values of $I_0 (=0.065)$ and $I_{\text{cat}} (=0.0046)$ measured over the Pt/ SiO_2 (Figure 1) were used to define the base parameters of a set of calculations giving the values of the Matyshak–Krylov function $MK(R, R_\infty)$ (eq 5.1), the Kubelka–Munk function $f(R')$ (eq 1) and the absorbance $= \log 1/R'$ (eq 3). The calculations were actually made by varying R' values from 1 (corresponding to $R = R_\infty$, no adsorbate being present) down

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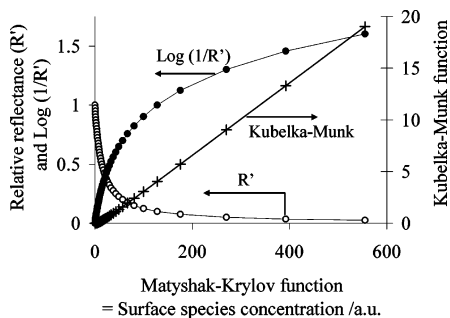


Figure 2. Theoretical values of (○) the relative reflectance R' , (●) $\log(1/R')$, and (+) the Kubelka–Munk transform $f(R')$ as a function of the Matyshak–Krylov function.

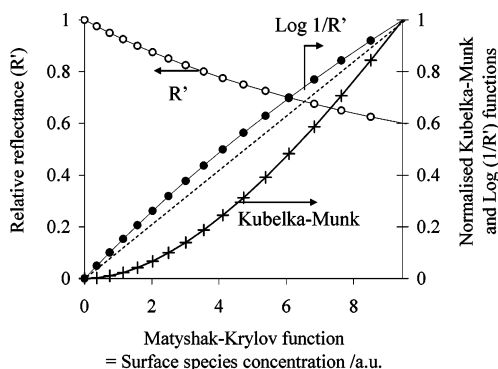


Figure 3. Detail of Figure 2, limited to relative reflectance R' values between 1 and 0.6. For the sake of comparing the shape of the curves, the Kubelka–Munk function $f(R')$ and absorbance = $\log(1/R')$ were normalized using the corresponding value of these functions at $R' = 0.6$. (the dashed line is an eye-guiding straight line).

to 0.05 (almost full absorption of the signal by the adsorbate) by steps of 0.05. Graphs were then plotted using the calculated values of the Matyshak–Krylov function $MK(R, R_{\infty})$ as x -coordinates (Figure 2 and 3), since $MK(R, R_{\infty})$ is supposed to be proportional to the surface coverage of the adsorbate (see Theory section). The cases corresponding to R' values lower than 0.6 and comprised between 1 and 0.6 (detailed on Figure 3) are discussed separately. The R' value of 0.6 was arbitrarily chosen as it corresponded to the R' value at full coverage of Pt by CO in the example described in Figure 1.

For R' values lower than 0.6, the Kubelka–Munk function $f(R')$ was essentially a linear function of $MK(R, R_{\infty})$, while the absorbance = $\log(1/R')$ yielded a markedly curved plot (Figure 2). Therefore, it can be concluded that the Kubelka–Munk function is the most suited representation of the coverage of surface species over this range of relative reflectance values.

For R' values comprised between 1 and 0.6 (Figure 3), the normalized values of $f(R')$, $\log(1/R')$ and a straight line (dashed line) were reported (normalized values were used for the sake of facilitating the comparison of the line shapes). Neither the Kubelka–Munk function nor the absorbance was a perfect straight line (see the offset with respect to the dashed line), yet the absorbance was clearly the closest to it. Note that the Kubelka–Munk function exhibited a marked change of slope over this range of R' values, stressing that the very low adsorbate surface concentrations are underrepresented with this function. Therefore, it can be concluded that the absorbance is the most suited representation of the coverage of surface species over this range

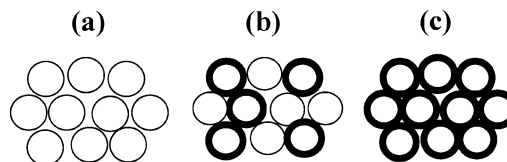


Figure 4. Schematic representation of some of the mixtures used for the determination of the relationship between the DRIFTS signal of CO(ads) and the proportion of adsorption sites in the sample: (a) SiO₂ support only, (b) 50 wt% of SiO₂ and 50 wt% of Pt/SiO₂, and (c) Pt/SiO₂ only. Only the Pt-based material will adsorb CO, and therefore the relative surface coverage of the various mixtures is simply given by the proportion of Pt/SiO₂.

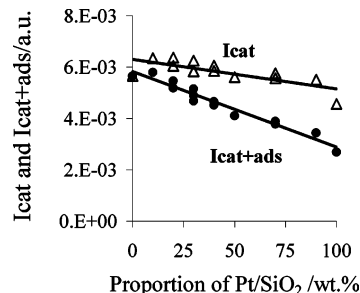


Figure 5. MCT detector intensity I_{cat} (Δ) and $I_{\text{cat+ads}}$ (\bullet) measured at 2080 cm^{-1} over various mixtures made of SiO₂ and Pt/SiO₂. The intensity were measured at 20 °C under Ar for the case of I_{cat} and under 1%CO/Ar in the case of $I_{\text{cat+ads}}$.

of relative reflectance values, contrary to the case relating to $R' < 0.6$.

CO Adsorption on SiO₂ + Pt/SiO₂ Mixtures. A set of experiments was designed to evaluate the relevance of the model and theoretical plots derived above. Pure SiO₂ and a 2% Pt/SiO₂ catalyst (made using the same silica support) were mixed according to different proportions to create mixtures (Figure 4) that would yield a different apparent surface concentration of Pt-adsorbed carbonyl groups when the mixture was exposed to CO.

This approach is valid as long as the absorptivity and scattering coefficients of the various mixtures are not significantly different. This point was assessed by comparing the DRIFTS intensity value I_{cat} at the wavenumber of interest (i.e., 2080 cm^{-1}) collected over the mixtures before exposure to CO (Figure 5). The intensity collected over the various mixtures remained similar, although the signal decreased gradually with increasing proportions of Pt/SiO₂, stressing that the mixture-based method used here is only approximate. The intensity $I_{\text{cat+ads}}$ collected over the various mixtures in the presence of CO is also reported in Figure 5. The drop of intensity due to the carbonyl absorption was significantly greater than that due to the variation of the composition of the solid (as indicated by the difference in the slope of the two best fit lines), emphasizing that the absorption by the adsorbate was the main origin of the signal decrease.

Some datapoints were measured two or three times (by reloading an identical sample in the DRIFTS cell sample holder) and the spread of the intensity values obtained was noticeable (Figure 5). It stresses the difficulty of obtaining identical sample packing in DRIFTS analysis¹² using this type of commercial equipment, which do not comprise a full integration sphere. For the sake of completeness, the absorbance (= $\log(1/R)$) spectra of the pure SiO₂, pure Pt/SiO₂, and a 50/50 mixture of the two

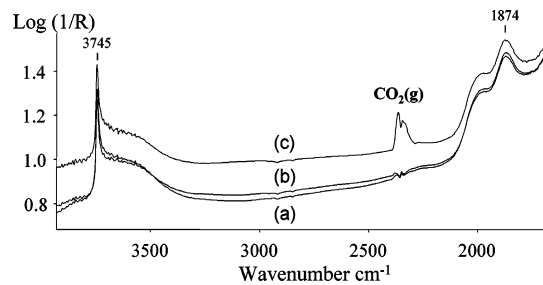


Figure 6. DRIFTS spectra of (a) the pure SiO₂ support, (b) a mixture made of 50 wt% SiO₂ and 50 wt% of Pt/SiO₂, and (c) the pure Pt/SiO₂ catalyst under Ar at 20 °C. A mirror signal was used as reference. (Note: the CO₂ band observed was due to the ambient atmosphere).

materials are given in Figure 6). The typical features of silica samples were observed, e.g., the OH stretching band of unperturbed silanol groups at 3745 cm⁻¹ and silica overtone backbone vibrations at 1874 cm⁻¹. No added features could be observed on the Pt/SiO₂-containing samples.

The various transforms of the DRIFTS intensity obtained in the presence of CO over the pure SiO₂, pure Pt/SiO₂, and a 10/90 mixture are shown in Figure 7. The main band observed at 2080 cm⁻¹ was related to linearly bound CO(ads), while a weaker band was also observed at 1800 cm⁻¹, due to bridged CO(ads). As indicated earlier, the relative reflectance R' at 2080 cm⁻¹ was ca. 60% over the pure Pt/SiO₂, while R' was ca. 90% over the SiO₂-rich mixture and essentially 100% over the pure SiO₂ (Figure 7a). Note that signal due to gas-phase CO was observable, but its contribution at 2080 cm⁻¹ was negligible. The corresponding absorbance = log 1/ R' plots are shown in Figure 7b, which actually displayed similar features. The corresponding Kubelka–Munk transform $f(R')$ are shown in Figure 7c. It is obvious that the shape of the spectra are quite different from those presented in Figure 7a and 7b, as only the most intense band remains observable. This is a well-known feature of the Kubelka–Munk transform that disproportionately emphasizes high-intensity bands.

The values of the relative reflectance R' , absorbance = log 1/ R' and Kubelka–Munk transform measured at 2080 cm⁻¹ over the different mixtures under CO are reported in Figure 8. The relative reflectance varied from 1 (on pure SiO₂) to ca. 60% (on pure Pt/SiO₂), similarly to the model plots described in Figure 3. The line shape similarity between the model (Figure 3) and the experimental (Figure 8) plots associated with the absorbance and Kubelka–Munk functions is obvious, in spite of the experimental errors and the approximations associated with this method. As expected from the model, the absorbance was most proportional to the concentration of surface carbonyl over this range of R' values. The Kubelka–Munk function particularly underestimated the adsorbate concentrations at R' values close to 100%, as compared to those in the range 80% < R' < 60%. An approximately 3-fold higher slope of the tangent to the Kubelka–Munk curve was observed in the latter case.

The value of the Matyshak–Krylov function MK(R, R_{∞}) at 2080 cm⁻¹ was also plotted as a function of the proportion of Pt/SiO₂ in the mixture (Figure 9). The function MK(R, R_{∞}) appeared quite linear with respect to the proportion of Pt in the system, which supports the suggestion that MK(R, R_{∞}) is proportional to the surface concentration of carbonyl species, as proposed by Maty-

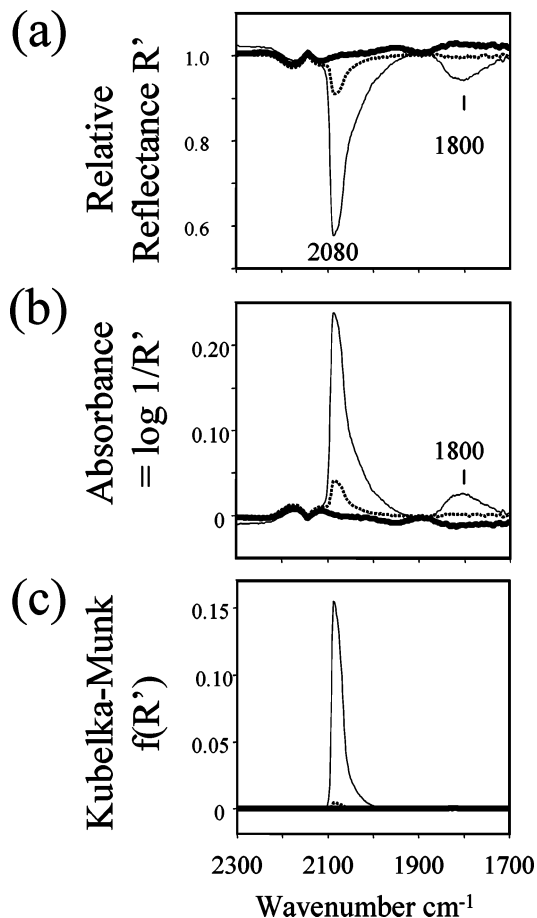


Figure 7. (a) Relative reflectance R' , (b) absorbance (= log 1/ R'), and (c) Kubelka–Munk $f(R')$ transform of the in situ DRIFTS spectra measured over SiO₂ (thick line), 90% of SiO₂ + 10% of Pt/SiO₂ (dashed line), and Pt/SiO₂ (thin solid line) at 20 °C under 1% CO/Ar. The reference signal used was that of the sample before exposure to CO(g).

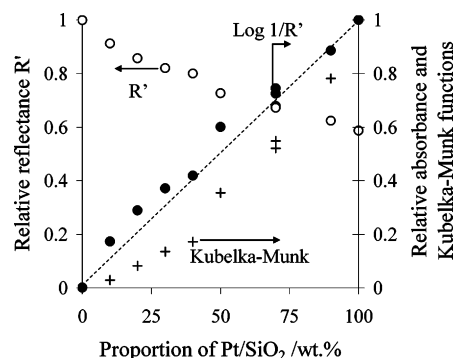


Figure 8. Values of the (○) relative reflectance R' , (●) absorbance = log (1/ R'), and (+) Kubelka–Munk $f(R')$ as a function of the proportion of Pt/SiO₂ in the SiO₂ and Pt/SiO₂ mechanical mixtures. The corresponding DRIFTS intensities were measured at 2080 cm⁻¹, which corresponded to the maximum of adsorption of Pt-bound carbonyl species. The data were collected at 20 °C under 1% CO /Ar.

shak and Krylov.³³ This plot suggests that the method employed here is actually rather precise, despite the fact that absorption and scattering properties were somewhat different for each sample (see I_{cat} , Figure 5).

It is interesting to note that van Every and Griffiths carried out a related investigation in which the Kubelka–Munk transform

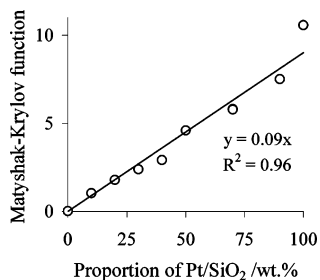


Figure 9. Values of the Matyshak–Krylov function $MK (R, R_{\infty})$ as a function of the proportion of Pt/SiO₂ in the SiO₂ and Pt/SiO₂ mechanical mixtures. The $MK (R, R_{\infty})$ function was calculated at 2080 cm⁻¹, which corresponded to the maximum of adsorption of Pt-bound carbonyl species.

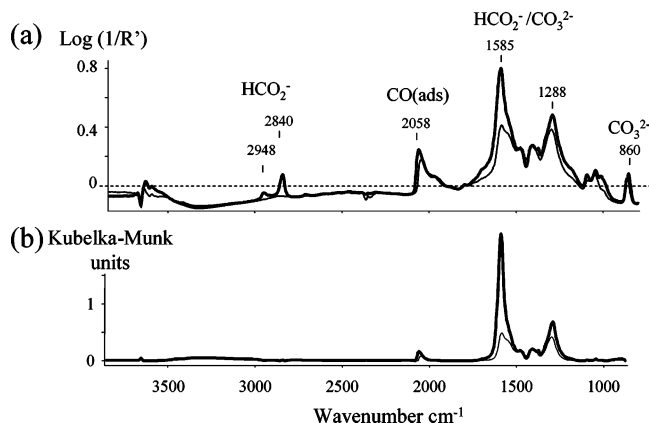


Figure 10. In situ DRIFTS spectrum reported in (a) absorbance = $-\log R'$ and (b) Kubelka–Munk units of a 2 wt% Pt/CeO₂ at steady-state under 1% CO₂ + 4% H₂ in Ar (thick line) and after 3 h in Ar (thin line). $T = 250$ °C. The sample under Ar before any contact with the reaction mixture was used as reference.

of carbonyl species adsorbed on Rh-containing catalyst was plotted as the function of the concentration of adsorbed CO.¹² The authors varied the carbonyl concentration by pulsing small quantities of CO in the DRIFTS cell. This mode of operation led to some other types of difficulties. First, the DRIFTS signal appeared to change with time because of a redistribution of the carbonyl throughout the sample, not all of which being probed by the IR beam.¹² Second, the total pressure of the cell also led to a modification of the sample packing and the position of the sample surface, changing the point of focus of the DRIFTS beam and the sample scattering coefficient.¹⁴ It was also proposed that nonlinearity effects could have been due to a modification of the carbonyl absorptivity with increasing surface coverage.¹² In conclusion, the adsorption technique reported by Griffiths et al.¹² also suffered from intrinsic biases in the determination of the DRIFTS signal versus surface concentration plot, as does the method used in the present work.

Formates Adsorbed on CeO₂. The data used in this section are related to a study of the reverse water-gas shift (RWGS) reaction over a Pt/CeO₂ catalyst published elsewhere.²⁸ Some absorbance plots already published in ref 28 are given again here and replotted in the Kubelka–Munk mode with a view at comparing these two modes of data analysis. Figure 10a shows the absorbance spectrum obtained under RWGS (thick line), which clearly shows the presence of formate species (combination band at 2948 cm⁻¹ and CH stretching at 2840 cm⁻¹), carbonyls at

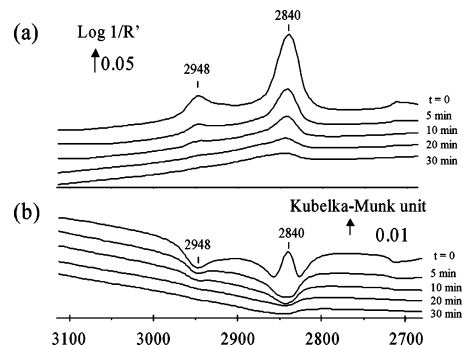


Figure 11. In situ DRIFTS spectra reported in (a) absorbance = $-\log R'$ and (b) Kubelka–Munk units of the 2 wt% Pt/CeO₂ at various times on stream under Ar at 250 °C. The sample was previously treated for 1 h under 1% CO₂ + 4% H₂ in Ar. The same sample under Ar was used as reference. The spectra were spread vertically for the sake of clarity.

2058 cm⁻¹, and carbonates (out-of-plane bending at 860 cm⁻¹). The bands in the region 1800–1000 cm⁻¹ were a complex superimposition of carbonate, formate, and carboxylate species and essentially impossible to deconstruct. The surface concentration of formate species was essentially nil after a 3 h purge in Ar, while the concentration of carbonyls and carbonates hardly changed. Plotting these data in Kubelka–Munk mode (Figure 10b) dramatically decreased the relative intensity of the weakest bands.

The detail of the wavenumber region around 2900 cm⁻¹ is given in Figure 11 (the spectra were shifted vertically for the sake of clarity). It must be mentioned that the position of the baseline varied nonuniformly and in particular was negative in the absorbance mode (see datapoints below the dotted line in Figure 10a). This fact was mostly a result of the variation of the absorption and scattering properties of the catalyst following the introduction of the reaction feed (the reference spectrum was the sample under Ar). Despite the baseline shift, the absorbance spectra were clearly resolved and showed no apparent distortion (Figure 11a), as already noted by Griffiths.³⁵ On the contrary, the formate bands at 2948 and 2840 cm⁻¹ were no longer observable for most of the Kubelka–Munk spectra reported, and peak inversions were also observed (Figure 11b). This set of data show how difficult the treatment of data in Kubelka–Munk units is, especially when baseline shift occurs,^{10,36} which is common during in situ study of catalytic materials. While baseline corrections are possible for Kubelka–Munk plots as it was recently highlighted,²⁴ those would be particularly tedious for typical time-resolved spectrokinetic analyses, during which thousands of spectra may be collected.

The desorption/reaction of formate species present at the surface of the Pt/CeO₂ under Ar is expected to follow a first-order law, leading to a single-exponential curve (assuming that the reactivity of the surface does not vary with time, because of a gradual change of its oxidation state⁸). As a matter of fact, a straight line was obtained when the logarithm of the area of the formate band (derived from the absorbance plot, integrated over 2900–2800 cm⁻¹) was plotted as a function of time under Ar (Figure 12). It is remarkable that the linearity was maintained

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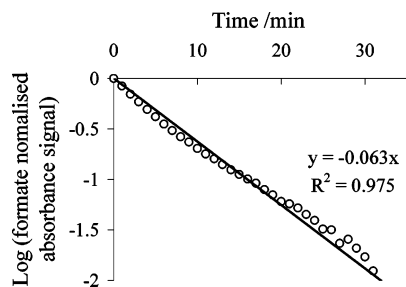


Figure 12. Logarithm of the normalized absorbance of the formate DRIFTS band measured over the 2 wt% Pt/CeO₂ under Ar. The sample was initially at steady-state under 1% CO₂ + 4% H₂ in Ar at 250 °C. The absorbance values corresponded to the area of the absorbance peak between 2900 and 2800 cm⁻¹ and were therefore intrinsically baseline-corrected.

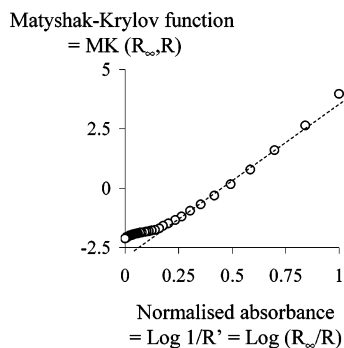


Figure 13. Relation between the Matyshak–Krylov function $MK(R, R_\infty)$ and the normalized absorbance $= \log 1/R' = \log (R_\infty/R)$ of the formate species during the desorption experiment described in Figures 10 and 11. The single scan intensity values at 2840 cm⁻¹ were used for the determination of $MK(R, R_\infty)$, without any baseline correction. The absorbance values corresponded to the area of the absorbance peak between 2900 and 2800 cm⁻¹ and were therefore intrinsically baseline-corrected.

down to 1/100th of the initial area value. Such first-order processes have also been observed during the isotopic exchange of formates during steady-state isotopic kinetic analyses of the WGS reaction.³⁷ The data plotted in the Kubelka–Munk mode were of course not directly useable and were therefore not processed. These data show the overwhelming advantage of using the absorbance ($= \log 1/R'$) when dealing with weak bands and/or for system showing baseline drifts.

The fact that the absorbance transform of the formate DRIFTS signal decay followed so closely a single-exponential law (Figure 12) suggests that the absorbance was exactly proportional to the adsorbate surface concentration over this range of data. Therefore, the corresponding data were used to plot the Matyshak–Krylov function, which is expected to be proportional to the adsorbate surface concentration,³³ as a function of the absorbance (Figure 13). The linearity of the plot was satisfactory for a large proportion of the desorption process, i.e., from the initial (normalized) adsorption of 1 down to 0.25. The plot thereafter varied in a nonmonotonous manner, possibly due to the fact that the Matyshak–Krylov values were not baseline-corrected, contrary to the absorbance values. The correction of baseline DRIFTS in the case

of Matyshak–Krylov data implies correcting directly the single scan spectrum, which is probably not straightforward, if possible. Therefore, this observation suggests that the baseline-corrected absorbance DRIFTS data are actually a more practical representation of the adsorbate surface concentration than the non-corrected Matyshak–Krylov transform.

Both the theoretical considerations and experimental work reported show that the absorbance $= \log 1/R'$ is the best and most practical linear representation of adsorbate surface concentration in the region of high relative reflectance ($R' > 0.6$), which is often the one of relevance to spectrokinetic studies. During such investigations, it can also be desirable to actually know the *specific* surface concentration of the adsorbate, e.g., in mol per surface area of the support or in weight fraction. This would be particularly useful to determine the specific rate of decomposition of surface intermediates. One way to do so involves the collection of calibration plots obtained via the preparation of standards of known surface concentrations.²³ We have done such calibration plots to determine the specific surface coverage of formates under WGS reaction conditions over a La-modified CeO₂³⁸ and a CeO₂-supported catalysts (in preparation). The standards were prepared by incipient wetness impregnation of the support. Despite the similarity in terms of composition and surface area of our samples, the slope of the calibration plot was significantly different for the two ceria-based materials, stressing that a calibration curve needs to be made for each material. Furthermore, McKenzie and Koenig have shown that slope-break could happen over similar plots, and therefore datapoints should not be extrapolated.²³

CONCLUSIONS

1. The intensity of adsorbates should be reported in the form of the Kubelka–Munk function $f(R')$ for the case of highly absorbing adsorbates (i.e., when the relative reflectance R' is lower than ca. 60%) to obtain DRIFTS data proportional to the adsorbate surface concentrations.
2. The intensity of adsorbates should be reported in the form of absorbance $= \log 1/R'$ for the case of poorly absorbing adsorbates (i.e., when the relative reflectance R' is higher than ca. 60%) to obtain DRIFTS data proportional to the adsorbate surface concentrations.
3. The use of absorbance ($= \log 1/R'$) yield peaks that are easily corrected for baseline shift, contrary to the cases of the Kubelka–Munk function $f(R')$ and Matyshak–Krylov function $MK(R, R_\infty)$.
4. In the case of the systems considered here, that is CO adsorbed on our Pt/SiO₂ and formates adsorbed on our Pt/CeO₂, we have shown that the Matyshak–Krylov function $MK(R, R_\infty)$ appears to be quite proportional to the adsorbate surface concentration, but is affected by baseline drifts.

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