Investigating catalytic reactions by DRIFTS spectroscopy and isotopic exchanges at the chemical steady-state: a quantitative approach.

F. C. Meunier*, J. Sirita, D. Rooney, S. Shekhtman, C. Hardacre, R. Burch,
School of Chemistry & Chemical Engineering, Queen's University Belfast, BT9 5AG, UK
*f.meunier@qub.ac.uk

Introduction

The investigation of the reactivity of molecules on catalysts by diffuse reflectance FT-IR spectroscopy (DRIFTS) has become widespread, due to the fact that powders (even strongly absorbing) can be directly used. Many investigations are being carried out under flow conditions with the simultaneous measure of the reaction rate (so-called *operando* conditions) with a view at relating the surface species coverage to the product formation rate. The technique is particularly powerful when isotopic transients (SSITKA) are used, allowing operating at the chemical steady-state and relating surface intermediates to gas-phase reaction products [1-6]. However, it is surprising to note that there is only a limited awareness of the actual requirements for a fully quantitative DRIFT analysis. This paper will review the quantitative aspect of DRIFT measurements and the checks and modifications that need to be carried out to ensure that kinetically meaningful rates are measured.

Materials and Methods

A commercial DRIFT cell (from Spectra-Tech®) was modified to ensure that no by-pass of the catalyst bed occurred and that the dynamic of the system was compatible with kinetic investigations. The original cell led to more than 90% by-pass of the bed by the feed when using a flow rate of 100 ml min^{-1}, as measured by the levelling-off to 10% of the conversion of CO in the presence of excess O_2. The original ceramic reactor was replaced with a custom-made ceramic reactor that was sealed with Teflon-tape against the metallic support. Total CO combustion could then be achieved low temperatures on the modified system, indicating that the bed by-pass was negligible.

The typical residence time distribution of the gaseous compounds in the cell was assessed monitoring the Kr signal during a switch from an Ar + Kr mixture to pure Ar. The distribution was nearly symmetric, with a mean value of ca. 6.8 s, a width of 3.5 s and an asymmetry of 2.2 s., showing that the cell was essentially behaving as a plug-flow reactor. A computational flow dynamics simulation allowed describing the flow pattern within the modified cell. The reaction rate for the water-gas shift reaction (WGS) over a gold catalyst was measured over our modified DRIFT reactor (in Belfast) and was found to be strictly identical to that measured in a tubular quartz plug-flow reactor at Tufts University[a].

Results and Discussion

The quantitative analysis of the surface coverage (θ) of adsorbates requires that a linear relation is found between a function of the DRIFT reflectance signal and θ. A detailed analysis of the mathematics of diffuse reflectance reveals that the Abs function (= - log Reflectance) is actually a better linear representation of θ than the Kubelka-Munk transform. This theoretical observation was supported by experimental evidences obtained measuring the DRIFT reflectance signal over a series of Pt-based silica mixtures during CO chemisorption.

The integration of the area of the DRIFT bands of surface species can be tedious, and a simple deconvolution is not always possible. This analysis is furthermore complicated when isotopic transient techniques are used [1-6], during which the number of surface species can be more than doubled. The integration of the surface concentration of an isotopomer can be carried out by integrating the IR bands on the very edge of the IR band, where other isotopomers would not significantly absord [1,2,5]. However, this technique typically results in poor signal-to-noise ratios. We have developed a least-square linear regression method that results in markedly improved signal-to-noise ratios, briefly presented in [6]. This method uses the initial (e.g. all non-labelled adsorbates) and final (e.g. all-labelled adsorbates) IR band regions corresponding to a given vibrational mode as a base for the deconvolution of the intermediate transient spectra [6]. New examples will show that this method can even be applied to ill-defined bands, as well as resolving kinetically different surface species absorbing in the same spectral region.

The typical analysis depth of DRIFTS is lower than a few hundreds microns and therefore scrutinize the catalyst only at the upper end of the sample bed. As a downward flow is usually used to prevent the very small particles being expelled from the bed, the DRIFT data relate to the front part of the bed. Any analytical devices located at the exit of the DRIFTS cell measures the composition of the effluent of the whole reactor. Data collected on our modified DRIFT cell allowed monitoring the exchange of CO_2 during SSITKA-type experiments at the bed front by DRIFTS and at the exit of the DRIFT cell by mass spectrometry. These CO_2 signals were found to be identical, showing that under differential conditions our DRIFT data can be directly related to the MS data measured at the cell exit. The occurrence of product readsorption will be discussed, as well as the utilisation of calibration curves to allow a fully quantitative determination of the absolute concentration of adsorbates.

Significance

This works demonstrates that experiments carried out in an appropriately modified and controlled commercial DRIFT cell combined with an advanced DRIFT signal integration and treatment yield fully quantitative information on the true steady-state reactivity of adsorbates.

References

1. Tibiletti, D., Goguet, A., Meunier, F., Breen, J., Burch, R. *Chem. Comm.* 1636 (2004).
2. Goguet, A, Meunier, F.C., Breen, J., Burch R. *J. Phys. Chem. B* 108, 20240 (2004).
3. Stevens, R.W., Chuang, S.S.C. *J. Phys. Chem. B* 108, 696 (2004).
4. Yang, Y., Disselkamp, R.S., Szanyi, J., Peden, C.H.F., Campbell, C.T., Goodwin, J.G. Rev. Sci. Inst. 77, 094104 (2006).
5. Tibiletti D, Goguet A, Reid D, Meunier FC, Burch R *Catal. Today* 113, 94 (2006).
6. D. Tibiletti, F.C. Meunier, F.C., Goguet, A., Reid, D. Burch, R., Boaro, M. , Vicario, M., Trovarelli, A. *J. Catal.* 244, 183 (2006).