



Review

The power of quantitative kinetic studies of adsorbate reactivity by operando FTIR spectroscopy carried out at chemical potential steady-state

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ABSTRACT

This paper reviews some of the aspects of combining in situ/operando infrared spectroscopy and kinetic studies. The strengths and limitations of various methods are discussed based on examples found in the literature and especially taken from the present author. A clear warning is made that qualitative or semi-quantitative analyses can easily result in unimportant surface species being mistaken for true reaction intermediates.

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1. Introduction

The improvement of the activity and selectivity of catalysts is a perpetual objective for researchers in catalysis and can rely on a number of approaches. While high-throughput combinatorial methods are raising a lot interest and finding some successes in heterogeneous catalysis [1], the understanding of reaction mechanism through detailed kinetic and spectroscopic studies is another proven approach to support catalyst development. The purpose of this report is to present some examples showing how insights into reaction mechanisms can be obtained from

combining in situ/operando spectroscopic data and kinetics (i.e. “spectrokinetics”).

The early seminal work of Tamaru et al. [2–5] and Matyshak et al. [6,7] from the 1960s and 1970s is first presented as typical examples of spectrokinetic studies. The input of Tamaru in the introduction of isotopic transient techniques [5] and the development of combined transmission FTIR and steady-state isotopic transient kinetic analysis (SSITKA) by Chuang and co-workers on a single bed reactor are acknowledged [8,9]. The extension of the method to diffuse reflectance spectroscopy (DRIFTS) is finally discussed in detail [10], in particular with respect to quantitative analyses, which are less straightforward in the diffuse reflectance mode as compared to the case of the transmission technique [11].

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From the recent examples taken from the work of the present author, the clearest warning about possible data misinterpretation comes from work on the water–gas shift (WGS) reaction over noble metals supported on oxides presented here as an example. The quantitative DRIFTS-MS-SSITKA technique proved invaluable in determining the true role of formates “seen by IR”, which turned out to be minor reaction intermediates (i.e. essentially spectators, belonging to a minor slow reaction pathway).

2. The historic bases of spectrokinetic analyses

Tamaru and co-workers investigated heterogeneous catalytic reactions by combining spectroscopic and kinetic data dating back to the 1960s [2–5]. The corresponding studies represented some of the first attempts to relate the concentration and reactivity of surface species to the rate of the reaction measured over the same catalyst. The water–gas shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, over base metal oxides was one of the simplest reactions investigated by these authors. This type of experiments was highly challenging at the time, bearing in mind the technological limitations of the equipment (e.g. using dispersive IR, since FTIR only become widespread much later [12]) and supply of high purity gases (e.g. CO was sometimes obtained from the decomposition of sodium formate by sulphuric acid and using a liquid nitrogen trap [4]). Custom-made cells had to be designed and built to carry out the spectroscopic and kinetic measurements.

It must be stressed that the reaction cell used by Tamaru and co-workers was actually made of two sections, each of those containing a catalyst bed. The first bed was used for the transmission IR analysis of a single wafer (e.g. with a mass of 300 mg) and the second bed contained a much larger mass of catalyst (e.g. 11 g) to ensure a measurable conversion [4]. The utilisation of a dual bed cell implies a non-negligible risk that each bed experienced different experimental parameters such as temperature and concentration gradients.

The decomposition rate of surface formates to CO_2 was compared to the rate of CO_2 production during the water–gas shift reaction (WGS) obtained over an MgO sample at 280 °C. The WGS rate was measured under a feed of CO and water in a recirculation mode. In a different experiment, the rate of formate decomposition to CO_2 was obtained by following the decay of the formate bands in an inert atmosphere for various initial surface coverages. The selectivity of formate decomposition (i.e. to CO or CO_2) was assessed by analysing the gaseous species formed by gas chromatography. The quantitative relation between IR band intensity and formate concentration was obtained via a calibration curve realised using reference samples derived from adsorption of known amounts of formic acid on the catalyst. The values of WGS rate and formate decomposition were sufficiently similar (Table 1) so that the formates seen by IR could be conclusively proposed as a main reaction intermediate (in other words, these formates seen by IR were part of the main reaction pathway).

This type of studies, based on a transient involving a change in the chemical potential of one or more of the chemical elements

present, assumes that the reactivity of the surface species is the same under steady-state reaction conditions and during experiments involving concentration changes. This is clearly not always the case [13] and will be discussed in more detail in the subsequent sections of the present review.

A large number of spectrokinetic studies were also carried out starting from the 1970s in the former USSR by Matyshak et al. [6]. A recent review gathering many examples of this work has been published in *Catalysis Today* [7]. In essence, these authors varied many experimental parameters (in particular reactant concentrations) for the reaction of interest and measured the consumption rate of the reactant(s), formation rate of the product(s) and the surface coverage of adsorbates observable by IR. A microkinetic model was then developed and the experimental and simulated variations of rates and surface coverages were compared to ascertain the model [7]. The procedure, leading to a possible reaction mechanism, appeared to be experiment- and time-intensive. Unfortunately, the methods used to carry out spectral decomposition were often unclear, while this point is often the bottleneck when complex spectra are considered. Other difficulties associated with the technique regarded the determination of molar absorption coefficients and, sometimes, the use of chemical potential transients (through changes of the overall concentration of some or all of the chemical elements involved in the reaction). In summary, the full microkinetic analysis combined with spectroscopy is an elegant method but clearly requires a significant amount of work and still some assumptions.

3. Operando and isotopic transient investigations of catalytic reactions

The collection and comparison of kinetic and spectroscopic data can be useful to gain some understanding of the mechanism of a catalytic reaction. However, data pertaining to different techniques are usually collected on separate apparatuses, each having its own reactor. The simultaneous collection of various spectroscopic data in a single reactor is currently receiving much attention as a means to overcome the possibility of differences in the actual experimental conditions prevailing in separate reactors [14–16]. In order to identify more focussed analytical techniques a new expression, i.e. “operando”, was put forward. The term “operando spectroscopy” refers to spectroscopic measurements of catalysts under working conditions with simultaneous on-line product analysis. This term was used in the literature starting from 2002 [17,18] with the aim to distinguish work in which on-line activity measurement was performed alongside spectroscopic measurements (i.e. *operando*) from work in which only spectroscopic data were recorded (i.e. *in situ*). The on-line analysis of the reactor effluent is useful in many ways. Firstly, it allows collecting kinetic data that are directly related to the spectroscopic data simultaneously measured (whether the cell is behaving like an ideal reactor or not!). Secondly, it allows determining whether or not the activity data obtained in the *operando* reactor are kinetically meaningful by comparing those with data obtained in a conventional “ideal” reactor for accurate kinetic measurements.

Spectrokinetic analyses are often carried out under non-steady-state chemical conditions, that is the chemical potential of one or more of the elements present in the system is modified in a step-wise, pulse or periodic manner [19,20]. This may yet sometimes results in flawed conclusions when the catalyst oxidation state varies depending on the feed composition (see the following section).

Spectroscopic studies are more powerful when combined with isotopic transient methods (SSITKA [21,22]), which allow operating at the chemical (potential) steady-state. To our knowledge, Chuang and co-workers were the first to combine (transmission)

Table 1

Comparison of the rate of formate decomposition to $\text{CO}_2 + \text{H}_2$ over MgO at 280 °C and the corresponding WGS rate. Both sets of data were obtained for the same surface coverage of formates [from reference [4], Reproduced by permission of The Royal Society of Chemistry].

Formate fractional surface coverage	Rate of formate decomposition to $\text{CO}_2 + \text{H}_2$ ($\text{mm}^3 \text{g}^{-1} \text{h}^{-1}$)	Rate of the water–gas shift reaction ($\text{mm}^3 \text{g}^{-1} \text{h}^{-1}$)
0.06	17	11
0.07	25	23
0.08	37	31

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