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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.

**Contents**

## 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, $CO + H_2O \rightarrow CO_2 + H_2$, 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 (WGSR) obtained over an MgO sample at 280 °C. The WGSR 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 WGSR 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.

**Table 1**
Comparison of the rate of formate decomposition to $CO_2 + H_2$ over MgO at 280 °C and the corresponding WGSR 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 $CO_2 + H_2$ ($mm^3\,g^{-1}\,h^{-1}$) | Rate of the water–gas shift reaction ($mm^3\,g^{-1}\,h^{-1}$) |
|---|---|---|
| 0.06 | 17 | 11 |
| 0.07 | 25 | 23 |
| 0.08 | 37 | 31 |

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)

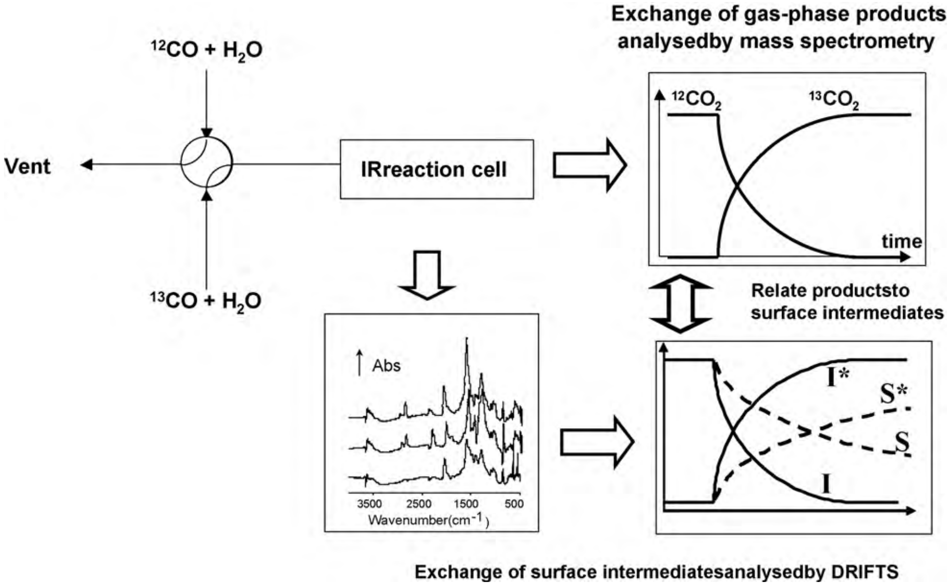

**Fig. 1.** Schematic representation of the IR-MS-SSITKA technique for the *operando* investigation of catalytic reactions. This technique is based on the utilisation of a single reactor (i.e. IR reaction cell) and allows following the kinetic of isotope exchange of both gas phase products P (by MS) and surface intermediates (by transmission IR or DRIFTS) during a SSITKA-type experiment. The surface species noted I represents a true reaction intermediate, while the surface species S is a "spectator" (better called a minor intermediate). I* and S* are the corresponding labeled surface species.

FTIR and isotopic transient kinetic measurement using a single bed reactor [8,9,23] (contrary to Tamaru's work described in Section 2 [5]). A schematic representation of the IR-SSITKA-MS method is given in Fig. 1. The use of the SSITKA method allows assessing the reactivity of surface species with respect to the formation of a reaction product under steady-state conditions in terms of chemical potentials of all the elements present (more details on the SSITKA technique can be found elsewhere [21,24]). In brief, this technique consists in replacing one of the reactants (e.g. $^{12}$CO) by an isotopomer (e.g. $^{13}$CO) during reaction and following simultaneously the exchange of the labeled reaction product (here $^{13}$CO$_2$) by mass spectrometry and the surface species (e.g. $^{13 \text{ or } 12}$C-containing carbonyl and formates) by IR. The IR bands of the surface species typically shift in wavenumbers during the analysis, and various integration methods (e.g. area integration or spectrum linear decomposition [38]) can be used to quantify accurately the band heights or areas [38].

Surface species observable by IR can only be part of the main reaction pathway if those globally isotopically exchange at least as fast as the reaction product does in the gas phase (e.g. species I in Fig. 1). Note that a true reaction intermediate could possibly isotopically exchange faster than the corresponding gas-phase product would do, if the latter readsorbs many times on the catalyst surface (without reverse reaction to the reactant, as in a chromatographic effect) or on the reactor walls before leaving the reactor [30]. Such artefacts are possible because the isotope exchange of the surface species is measured directly in (through) the reactor bed, while gas-phase exchange is typically measured at the reactor exit. An obvious improvement to the technique would be to locate the capillary inlet of the mass spectrometer directly into the reactor bed. A significantly slower isotopic exchange or no exchange at all indicates a minor reaction intermediate (i.e. species involved in minor reaction pathway) and a spectator species, respectively (e.g. species S in Fig. 1). A nice example of formates seen by IR as being spectator species during the water–gas shift reaction was recently reported by Efstathiou and co-workers [25]. The analysis of the surface and gas-phase exchange curves can become difficult when complex reaction pathways involving parallel and/or consecutive steps with similar rates are involved. More in-depth mathematical analyses of the exchange curves as described for SSITKA work [21] is required to attempt drawing conclusions in this case.

This *operando* IR-SSITKA-MS method using a single catalytic bed allows the characterisation by IR spectroscopy of the surface of the very same catalyst particles that are responsible for the catalytic activity measured at the exit of the cell by gas chromatography or mass spectrometry. Chuang and co-workers investigated, for instance, the details of the hydroformylation (CO + ethene) [9] and CO + NO [26] reactions. The authors could support the role of various surface species (e.g. carbonyl) as reaction intermediates based on the comparison of the time constant of exchange of the gas-phase products and that of the surface species. The clear advantage of isotopic transient methods is that it makes possible monitoring the reactivity of adsorbates while still working at the chemical potential steady-state. Therefore, a constant catalyst chemical composition and a constant surface coverage of the various species present under true reaction conditions is ensured (in the sense that isotopomeric species are of the same chemical nature).

The group at Queen's University Belfast was the first to report same type of isotopic transient work based on a DRIFTS cell used as a single bed reactor [10]. Note that mass transport limitations may occur with the sometimes thick wafers used in transmission IR mode and that the temperature control can also be difficult, as it is for DRIFTS cells at high reaction temperatures. The advantage of the transmission mode is that essentially the entire sample volume is being probed during the IR analysis (except for boundary regions of the wafer and/or regions hidden by the sample holder). In the case of DRIFTS, using differential conditions (i.e. conversion lower than 10%, leading to a near-homogeneous bed) must be ensured if quantitative or even only qualitative work is to be carried out. This is because only the top fraction of the sample is probed, typically less than 200 $\mu$m in depth [27] for most poorly absorbing materials. The analysis depth will of course be shorter if strongly absorbing bodies such as metals are present.

## 4. Importance of using chemical steady-states unravelled by isotopic techniques

An example of DRIFTS-SSITKA-MS experiment is given here with respect to the reverse water–gas shift (RWGS) reaction [10]:

$$\text{RWGS}: \quad CO_2 + H_2 \Rightarrow CO + H_2O \qquad (1)$$

The importance of using chemical potential steady-state conditions for the study of the reverse water–gas shift reaction over Pt/$CeO_2$ was highlighted during our investigation simply by comparing the time constant associated with the removal of surface species during (i) a purge in an inert gas and (ii) during an isotope exchange [28,13]. Our data clearly showed that the reactivity of surface species, in particular that of carbonate species, was markedly different under these two gas streams (Fig. 2). We believe that the difference of reactivity observed was related to the difference in the oxidising/reducing nature of the feed, which altered the oxidation state of the ceria surface, which in turn modified the strength of the adsorbate bonding to the ceria surface [29].

Another example of the importance of using chemical steady-state was also recently reported by Mims and co-workers in the case of the synthesis of methanol over Cu/$SiO_2$ catalysts [30]. The authors measured the rate of decomposition of the Cu-bound formates formed under CO/$H_2$ mixtures. The formate decomposition rate was up to 3-fold lower in the case of a CO-free feed, as compared to the case of the full CO/$H_2$ mixture. Note that in this particular example [30], formates "seen by IR" were conclusively shown to be main reaction intermediates (i.e. belonging to the main reaction pathway). The lower reactivity of formates observed under the CO-free feed was assigned to the loss of co-adsorbate effects. The two examples reported above strongly emphasise that not using chemical potential steady-state conditions may lead to flawed kinetic investigations.

## 5. DRIFTS as a quantitative analysis technique

Diffuse reflectance FTIR spectroscopy (DRIFTS) [31–33] is increasingly being used as a means to investigate the reactivity of surface species under reaction conditions, but it is usually considered only as a qualitative technique. However, it was demonstrated that DRIFTS spectroscopy can be an accurate quantitative tool for operando studies, providing that an appropriate analytical transformation of the diffused intensity is used (i.e. in most cases the pseudo-absorbance rather than the Kubelka–Munk function [34]) and that a calibration curve relating band intensity to adsorbate concentration is available [35]. These two aspects are briefly discussed now.

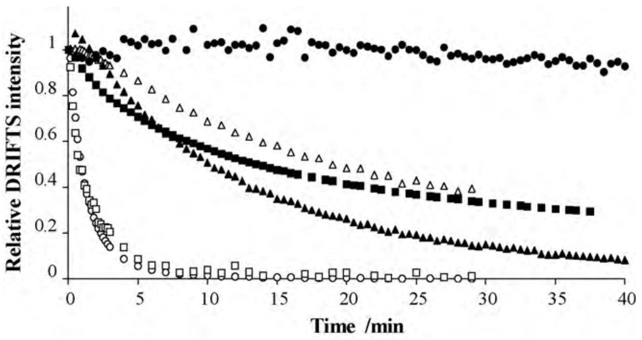

**Fig. 2.** Relative intensity of the IR bands of the formate (▲, △), carbonyl (■, □) and carbonate (●, ○) species as a function of time on stream under Ar (solid symbols) and under RWGS stream containing $^{13}CO_2$ (open symbols). The sample was at steady-state in 1% $^{12}CO_2$ + 4% $H_2$ and $T$ = 498 K before switching to either Ar or the $^{13}CO_2$-containing feed (Reprinted from reference [28], © Elsevier Inc.).

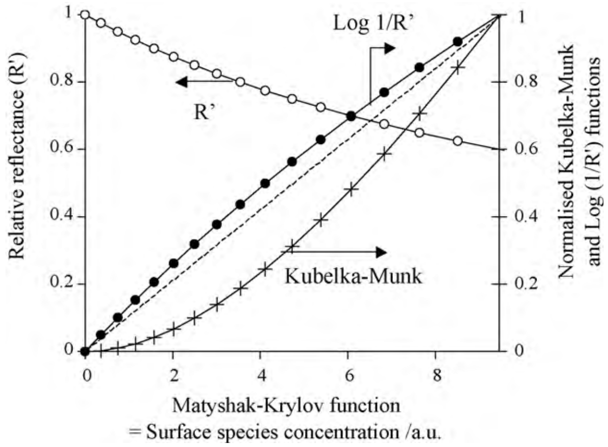

**Fig. 3.** Theoretical values of (○) the relative reflectance $R'$, (●) $\log(1/R')$ and (+) the Kubelka–Munk transform $F(R')$ as a function of the Matyshak–Krylov function, which is proportional to adsorbate concentration (Reprinted from reference [34] with permission, © ACS Publications).

There is a widespread misconception that the IR signal measured in the diffuse reflectance mode of species adsorbed at surfaces must always be reported as Kubelka–Munk units. In fact, a different expression has been proposed by Mathyshal and Krylov to account for the concentration of adsorbates [36]. Based on this work, we have shown [34] that the (pseudo-)absorbance is a more linear function of the surface concentration than the Kubelka–Munk function in the range of relative reflectance comprised between 100 and 60% (Fig. 3). This range of relative reflectance is pertinent to most DRIFTS studies of surface species, for which the signal loss due to the absorption by the adsorbed species is weak. The use of the absorbance function also overcomes the problem associated with baseline drifts during measurements [34]. It is only in the case of low values of reflectance that using the Kubelka–Munk transform may be more appropriate.

Further evidence that absorbance units are most appropriate when investigating surface species by DRIFTS is given by the data reported in Figs. 4 and 5, which relate to the decomposition of surface formates species during the reverse water–gas shift reaction over a ceria-based catalyst [34]. The disappearance of the formate bands was followed after replacing the reaction feed

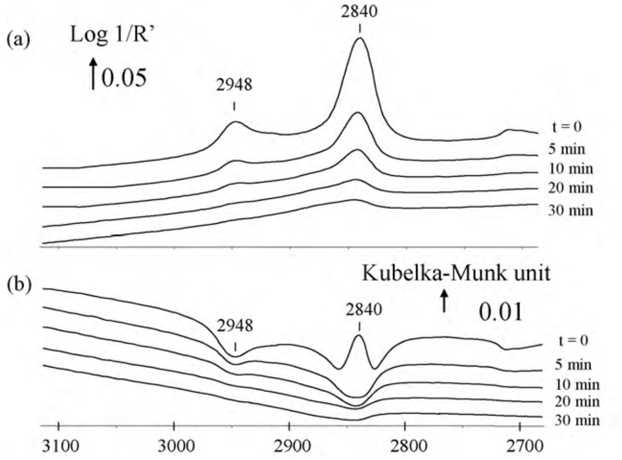

**Fig. 4.** In situ DRIFTS spectra reported in (a) absorbance = −log $R'$ and (b) Kubelka–Munk units of a 2 wt.% Pt/$CeO_2$ at various times on stream under Ar at 250 °C. The sample was previously treated for 1 h under 1% $CO_2$ + 4% $H_2$ in Ar. The same sample under Ar was used as reference. The spectra were spread vertically for the sake of clarity (Reprinted from reference [34] with permission, © ACS Publications).

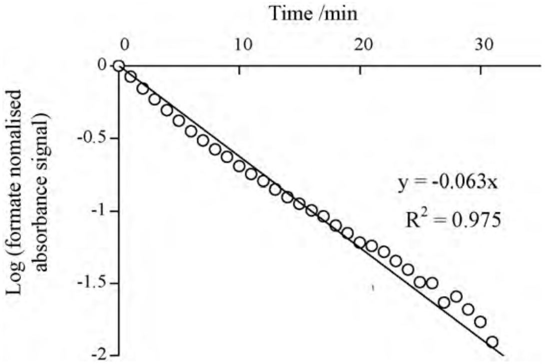

**Fig. 5.** Logarithm of the normalised absorbance of the formate DRIFTS band measured over a 2 wt.% Pt/$CeO_2$ under Ar. The sample was initially at steady-state under 1% $CO_2$ + 4% $H_2$ in Ar at 250 °C. The absorbance values corresponded to the area of the absorbance peak between 2900 and 2800 $cm^{-1}$, and were therefore intrinsically baseline-corrected (Reprinted from reference [34] with permission, © ACS Publications).

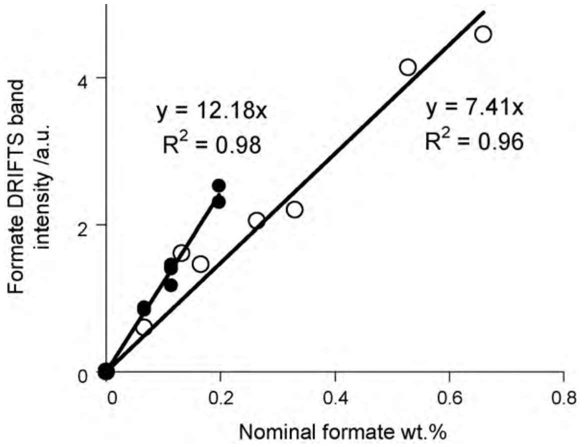

**Fig. 6.** Calibration plots relating the area of the formate CH stretching DRIFTS band to the nominal formate loading of the $CeZrO_4$ (○) and $CeO_2$ (●) supports impregnated with sodium formate (Reprinted from reference [11], © Elsevier Inc.).

with pure argon. The formate bands became distorted when the Kubelka–Munk units were used, because of a slight baseline shift (Fig. 4b). On the contrary, the formate bands kept their expected shape when the intensity reported was based on absorbance (Fig. 4a). An almost perfect exponential decay was observed, as expected in the case of first order processes, since the corresponding semi-logarithmic plot yielded a straight line (Fig. 5). As a consequence, the absorbance units were typically used during our investigations whenever any quantitative work was carried out [34].

More evidence that the pseudo-absorbance is an appropriate transform of the signal intensity for high reflectance values has been recently reported by Bianchi and co-workers [37]. These authors were able to match data relating to CO adsorption on Cu and Ti cationic species measured both by transmission and diffuse reflectance modes. Bianchi et al. indicated that the relative reflectance needed to be higher than ca. 60% to obtain a meaningful quantification of the DRIFTS data through the use of the pseudo-absorbance. This range of pseudo-absorbance values (i.e. 100–60%), corresponding to the weak signal absorptions typically observed during adsorption and reaction over catalytic materials, is in agreement with the theoretical considerations previously reported by Meunier and co-workers [34].

Another common misconception is that DRIFTS work cannot lead to quantitative data, contrary to the case of transmission IR data. On the contrary, we were able to draw calibration curves to accurately quantify the concentration of formates (Fig. 6), using these curves to derive the concentration in mol/g of formates during our operando work [11,35]. The only obvious restriction to use of such calibration curves is that the catalyst bed must be homogeneous, as only the upper part of the sample volume is typically probed by this technique [27]. This implies that differential conditions must be used during catalytic measurements.

## 6. Operando studies using a DRIFTS reaction cell

Like any other reaction cells, a DRIFTS cell should be checked for kinetic relevance and possibly modified to correct any hydrodynamic flaw. We also showed that an appropriately modified DRIFTS cell reactor (by limiting bed by-pass in particular [38]) led to reaction rates identical to those measured in a linear quartz tube plug-flow reactor (Fig. 7) [35]. DRIFTS reactors are particularly suited for operando investigations since the catalyst powder can be used as such, whereas FTIR-transmission techniques require pressing wafers, which can lead to mass transport limitations and catalyst modifications.

The DRIFTS and mass spectrometry (MS) data collected during DRIFTS-MS experiments actually relate to different regions of the reactor. The DRIFTS data are often collected at the front (and top) part of the bed, while the MS data are collected at the exit of the cell, i.e. after the bed (Fig. 8a). If the evolution of the MS signal of reaction products during an isotopic switch is to be compared to the evolution of the DRIFTS intensity of surface intermediates, then the gas phase all along the catalyst bed should be homogeneous. This is to ensure that the variation of the gas-phase composition at the front of the bed, which directly relates to the surface species observed by the DRIFTS, is equivalent to that measured by MS after the bed. In an example treated here based on water–gas shift data, we are fortunate that the reaction product $CO_2$ can be observed both by using the DRIFTS signal and by the MS [38]. Note that the bands measured by DRIFTS are related to the surface species present in the upper layer of the catalyst bed (typically at less than 200 μm depth [27] for a total bed length of *ca.* 2 mm), while the signal of $CO_2$(g) is coming from both the same catalyst layer and the free volume above the bed (Fig. 8a).

The isotopic exchange of $CO_2$ was followed during a SSITKA-DRIFTS-MS experiment over the Pt/$CeO_2$ catalyst. The CO conversion was 10% in these conditions, ensuring differential conditions.

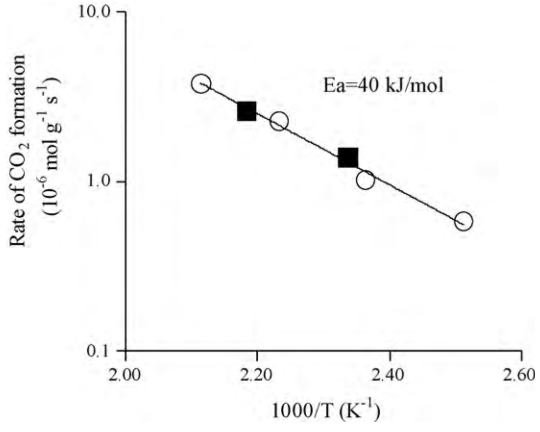

**Fig. 7.** Arrhenius plot relating to the rate of $CO_2$ formation measured over a gold-ceria-lanthana catalyst located (○) in a quartz plug-flow reactor and (■) in a modified DRIFTS cell. The feed was 2% $^{12}CO$ + 7% $H_2O$ in Ar or He (Reprinted from reference [35], © Elsevier Inc.).

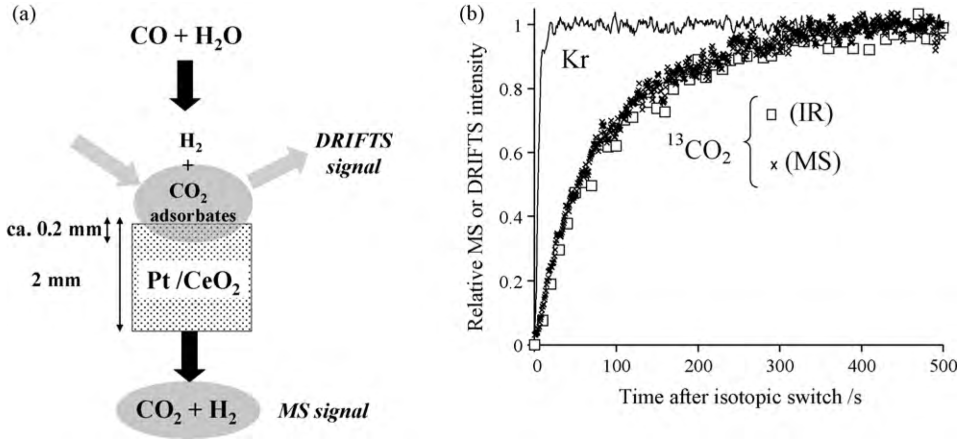

**Fig. 8.** (a) Schematic representation of the catalyst bed and the zone probed by the DRIFTS beam. The MS data are collected at the exit of the DRIFTS cell, i.e. after the bed. (b) Relative intensity of the Kr tracer (solid line), $^{13}CO_2$ measured by mass spectrometry (×) and $^{13}CO_2$ measured by the IR signal of the DRIFTS cell (□) following a $^{12}CO$–$^{13}CO$ isotopic switch under steady-state WGS conditions over a 2% Pt/$CeO_2$. $T$ = 473 K; feed: 1% $^{13}CO$ + 10% $H_2O$ in 2% Kr/Ar. The feed was 1% $^{12}CO$ + 10% $H_2O$ in Ar before the switch (Reprinted from reference [38], © Elsevier Inc.).

The evolution of the gas-phase $^{13}CO_2$ signals following the switch to the $^{13}CO$-containing feed is given in Fig. 8b. The MS signal of the Kr tracer is also reported for the sake of completeness. The Kr profile (Fig. 8b) (and that of the reactant CO, not shown here) was essentially a step-function in comparison with the $CO_2$ signals, indicating that the significant delay of the $^{13}CO_2$ response curve relative to the Kr one was due to chemical effects and not to mass transport effects (i.e. by the supply of labeled gas).

Note that this is not the case in the work reported by Jacobs and Davis [39], in which the isotopic exchange of surface and gaseous compounds is limited by the slow gradual introduction of the labeled gas (as the switching valve is located before the CO mass flow controller). The disadvantage of the latter technique is that all processes with a time constant lower than that of the supply of the labeled compounds (several minutes) will not be resolved, while the time constant of our method with this modified cell is ca. 7 s.

It is clear that the relative variations of the DRIFTS and MS signals associated with $^{13}CO_2$ (Fig. 8b) were identical, displaying an almost exponential increase with a 50%-exchange time of about 55 s. These data unambiguously show that the signal of the reaction product $CO_2$ measured by the MS after the catalyst bed perfectly corresponded to that measured at the bed entrance, which was measured using the DRIFTS signal. Therefore, the gas-phase profile in the thin (ca. 2 mm) catalyst bed was homogeneous, in the reaction conditions used here. This fact justifies the comparison of the curves obtained by DRIFTS for the surface species at the top of the bed and the curves obtained for the products of reaction by MS (or by any other analytical techniques) after the reactor, at least as long as differential conditions apply.

## 7. Operando SSITKA-DRIFTS-MS study of the RWGS: formates seen by IR as spectators based on time constant differences

An example of the application of the DRIFTS-MS-SSITKA technique is given below for the RWGS reaction [10]. Fig. 9 shows the typical DRIFTS spectra of formate, carbonyl and carbonate species during the isotope exchange $^{12}CO_2$ to $^{13}CO_2$ of the reactant. The replacement of $^{12}C$ with a heavier isotope led to a red-shift of most of the band wavenumbers associated with the surface species of interest. Note that we were able to integrate in an unequivocal manner the concentrations of the formate, carbonyl and carbonate species. Several methods can be used to quantify the exchange of each of the species, i.e. integration on band edges or, better, spectral decomposition based on the initial ($^{12}C$) and final ($^{13}C$) spectra [38].

The corresponding isotope exchange data of the surface species are reported in Fig. 10, which showed that carbonates and carbonyl species were typically half-exchanged in about 60 s. On the contrary the exchange time of formate species was much longer, i.e. about 11 min. The corresponding MS data showing the exchange of the gas-phase product CO are also shown in Fig. 10. It is clear that CO was exchanged at a timescale similar to that of the carbonyl and carbonates, and therefore these species are potentially main reaction intermediates, contrary to the formates. Formates should be named as minor intermediates, rather than spectator species, since those still exchanged and probably led to some CO, albeit at a much lower rate than the CO formed via the (unknown) main reaction intermediates.

## 8. Operando SSITKA-DRIFTS-MS study of the WGS

An example of DRIFTS-SSITKA-MS data relating to the water–gas shift (WGS, Eq. (2)) reaction over a 2% Pt–$CeO_2$ is given in Fig. 11 [40].

$$\text{WGS}: \quad CO + H_2O \Rightarrow CO_2 + H_2 \qquad (2)$$

The comparison of the isotope exchange curves of the reaction product (here $CO_2$) and of formates was more intriguing than that discussed in the previous section. The formate exchange was significantly slower than that of $CO_2$ at 160 °C, suggesting that formates were unimportant surface intermediates at these temperatures (Fig. 11). However, the exchange of these two species was essentially identical at 220 °C, suggesting that formates could potentially be a main reaction intermediate under these conditions.

The relevance of the formates seen by DRIFTS in the formation of $CO_2$ was ascertained by a quantitative comparison of the specific rate of $CO_2$ formation (measured by GC analysis of the DRIFTS cell effluents, which is more precise than the conversion derived from the MS data) and the specific rate of formate decomposition. The latter was calculated as the product of the formate concentration by the pseudo-first-order rate constant (noted $k$) of formate decomposition [11]:

$$\text{rate of formate decomposition} = k \times [\text{formate}] \times 100\%$$

The value of $k$ was determined from the formate exchange curve following the isotopic switch, which showed a first order decay (i.e. exponential curve) (see Fig. 11). The formate concentration was determined under reaction conditions via the calibration curves as described above [35,11]. The term 100% is introduced to indicate

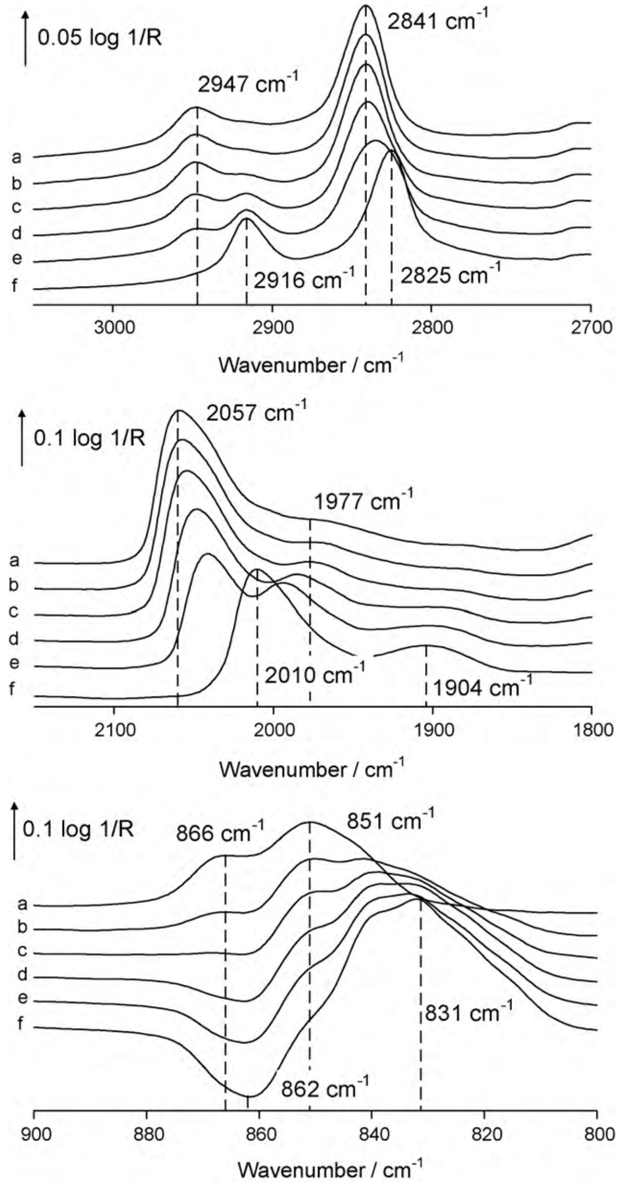

**Fig. 9.** Typical DRIFTS data of a DRIFTS-MS-SSITKA experiment during the RWGS over Pt-$CeO_2$: exchange of (top) formate, (middle) carbonyl and (bottom) carbonate species at various times after an isotope exchange $^{12}CO_2$ to $^{13}CO_2$. Feed: 1% $CO_2$ + 4% $H_2$ (Reprinted from reference [10], © ACS Publications).

that we arbitrarily assumed that the formate totally decomposed to $CO_2 + H_2$ and not at all to $CO + H_2O$. Therefore, our calculated formate decomposition rate yielded the upper limit of the rate of formate decomposition to $CO_2$, since it is likely that formates were not only decomposing to give $CO_2$, but instead gave a mixture of CO and $CO_2$. Even assuming that formates decomposed solely to $CO_2$, the rate of formate decomposition for our highly active Pt/$CeO_2$ WGS catalyst accounted for less than 10% of the total rate of $CO_2$ formation in the range of temperatures and experimental conditions used here (Fig. 12). Therefore, the formates seen by DRIFTS are minor reaction intermediates over this very active WGS catalyst; that is these species observed by DRIFTS are not part of the main reaction pathway. These observations stresses that the similarity of the isotope exchange time constant of formates and $CO_2$ is not a sufficient condition to guarantee that formates seen by DRIFTS are main reaction intermediates.

In some cases, formates seen by IR have been also considered essentially as "buffer" surface species [41]; whether those

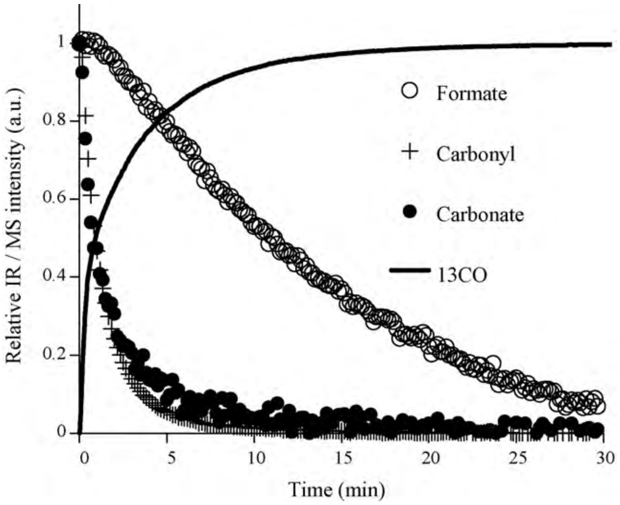

**Fig. 10.** Comparison of DRIFTS and MS data during a SSITKA experiment relating to the RWGS over Pt–$CeO_2$: the carbonate and carbonyl species are exchanged at a time scale similar to that of the reaction product CO and are potentially reaction intermediates. On the contrary, formates are clearly not main kinetic intermediates (Reprinted from reference [10], © ACS Publications).

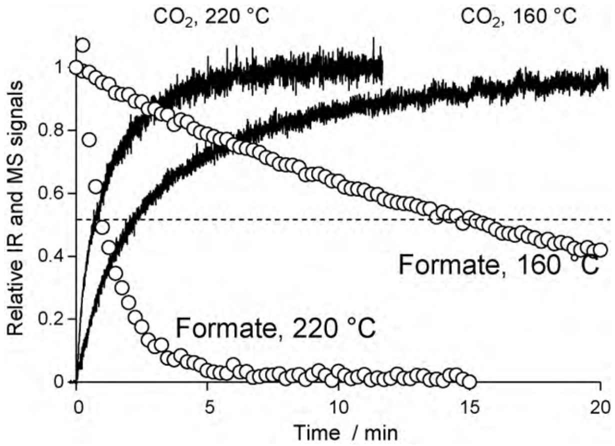

**Fig. 11.** Comparison of the relative exchange of the gas-phase $CO_2$ and surface formate species during an isotopic exchange over the Pt/$CeO_2$ at various temperatures. Feed: 2% $^{13}CO$, 7% $H_2O$ in Ar. The sample was initially at steady-state under the corresponding non-labeled feed (Reprinted from reference [40], © Elsevier Inc.).

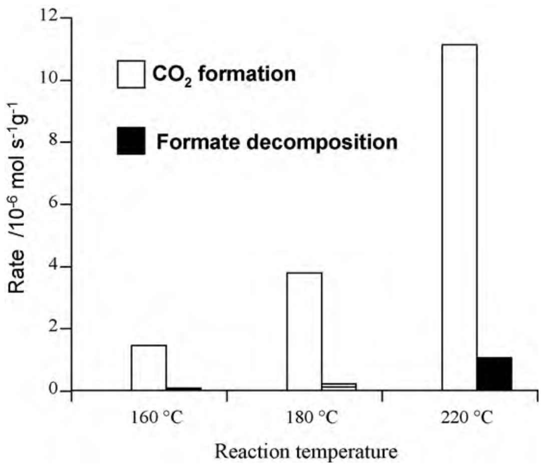

**Fig. 12.** Rate of $CO_2$ production and rate of formate decomposition over the Pt/$CeO_2$ at three different temperatures under 2% CO + 7% $H_2O$ in Ar (Reprinted from reference [11], © Elsevier Inc.).

participate or not to the main reaction pathway is unclear. In any case, while our work cannot indicate what the main WGS reaction pathway is, it certainly stresses that observing formates displaying some sort of reactivity is not a sufficient criterion to consider those as important reaction intermediates as proposed in many instances [42,43]. Of course, our conclusions are based on the samples that we investigated under our experimental conditions; therefore any extrapolation outside this system is hazardous. DFT-based work carried out both on ceria-supported noble metals and copper seems to favour the role of carboxyl species (HO–CO) as main reaction intermediate and excludes any significant role of formates [44,45]. The surface concentration of the carboxyl intermediates was estimated to be a thousand-fold lower than that of the "buffer" formates, suggesting that a direct observation of these short-lived species may be impossible by the current IR investigation techniques [44].

The main current limitation of the combined SSITKA and IR methods is that the decomposition pattern (i.e. selectivity to products) of a given adsorbate cannot be determined. Tamaru and later Iwasawa had used the decomposition of pre-adsorbed formates (from formic acid) on the catalyst to estimate their decomposition selectivity to $CO + H_2O$ or $CO_2 + H_2$. It is of course not always possible to prepare on request the expected surface intermediates and in addition their decomposition would then not be followed under chemical steady-state, which may lead to flawed interpretations.

## 9. Conclusions on the spectrokinetic investigation of catalytic reactions

The examples reported here show that combining spectroscopic and kinetic studies can greatly benefit to the understanding of heterogeneous catalytic reactions. The use of fully quantitative methods also revealed that "slowly" reacting surface species (i.e. essentially spectators) can sometimes be easily mistaken for true reaction intermediates. The conclusions derived from qualitative spectroscopic methods should therefore always be carefully considered and the corresponding limits of validity clearly defined. A reliable study of a catalytic system using spectroscopic tools should take into account the following points:

(i) It is crucial to check the kinetic relevance of the spectroscopic cell to be used for any operando work. Appropriately modified DRIFTS reaction cells can behave as true kinetic reactor.
(ii) DRIFTS analyses can be performed in a fully quantitative manner. In most cases, the absorbance units are more appropriate than Kubelka–Munk units.
(iii) Chemical potential steady-state must be used to determine the true operando reactivity of surface species, particularly for catalysts whose composition are affected by the reaction conditions.
(iv) The DRIFTS-SSITKA-MS is a truly operando technique and was proved useful in unravelling the (minor) role of formate species seen by DRIFTS during the water–gas shift reaction. This was achieved by calculating the rate of formate decomposition, which appeared to be significantly lower than that of $CO_2$ production. The nature of the true reaction intermediates under our experimental conditions remains unknown over these materials. Note that other types of formates, the concentration of which could be so small that the corresponding IR signal would be covered by that of the formates having a minor (spectator) role, cannot be excluded as main intermediates.

## References

[1] P. Cong, A. Dehestani, R. Doolen, D.M. Giaquinta, S. Guan, V. Markov, D. Poojary, K. Self, H. Turner, W.H. Weinberg, Proc. Natl. Acad. Sci. U.S.A. 96 (1999) 11077.
[2] K. Tamaru, Adv. Catal. 15 (1964) 65.
[3] K. Tamaru, J. Chem. Soc. Jpn. 87 (1966) 1007.
[4] A. Ueno, T. Onishi, K. Tamaru, Trans. Faraday Soc. 66 (1970) 756.
[5] K. Tamaru, Dynamic Heterogeneous Catalysis, Academic Press, New York/San Francisco, 1978.
[6] V.A. Matyshak, A.A. Ukharskii, A.A. Kadushin, Zhumal Prikl. Spektmskopii 24 (1971) 179.
[7] V.A. Matyshak, O.V. Krylov, Catal. Today 25 (1995) 1.
[8] M.W. Balakos, S.S.C. Chuang, G. Srivinas, J. Catal. 140 (1993) 281.
[9] R.W. Stevens, S.S.C. Chuang, J. Phys. Chem. B 108 (2004) 696.
[10] A. Goguet, D. Tibiletti, F.C. Meunier, J.P. Breen, R. Burch, J. Phys. Chem. B 108 (2004) 20240.
[11] F.C. Meunier, A. Goguet, C. Hardacre, R. Burch, D. Thompsett, J. Catal. 252 (2007) 18.
[12] A. Bell, Springer Ser. Chem. Phys. 34 (1984) 23.
[13] D. Tibiletti, A. Goguet, F.C. Meunier, J.P. Breen, R. Burch, Chem. Commun. (2004) 1636.
[14] A. Brucker, Chem. Commun. (2005) 1761.
[15] S.J. Tinnemans, J.G. Mesu, K. Kervinen, T. Visser, T.A. Nijhuis, A.M. Beale, D.E. Keller, A.M.J. van der Eerden, B.M. Weckhuysen, Catal. Today 113 (2006) 3.
[16] F.C. Meunier, M. Daturi, Catal. Today 113 (2006) 1.
[17] B.M. Weckhuysen, Chem. Commun. (2002) 97.
[18] M.O. Guerrero-Perez, M.A. Bañares, Chem. Commun. (2002) 1292.
[19] G.D. Pirngruber, J.A.Z. Pieterse, J. Catal. 237 (2006) 237.
[20] E.E. Ortelli, J. Wambach, A. Wokaun, Appl. Catal. A: Gen. 192 (2000) 137.
[21] S.L. Shannon, J.G. Goodwin, Chem. Rev. 95 (1995) 677.
[22] Y. Yang, R.S. Disselkamp, J. Szanyi, C.H.F. Peden, C.T. Campbell, J.G. Goodwin, Rev. Sci. Instrum. 77 (2006) 094104.
[23] G. Srivinas, S.S.C. Chuang, M.W. Balakos, AIChE J. 39 (1993) 530.
[24] A.M. Efstathiou, X.E. Verykios, Appl. Catal. A: Gen. 151 (1997) 109.
[25] C.M. Kalamaras, P. Panagiotopoulou, D.I. Kondarides, A.M. Efstathiou, J. Catal. 264 (2009) 117.
[26] R. Krishnamurthy, S.S.C. Chuang, M.W. Balakos, J. Catal. 157 (1995) 512.
[27] C. Mondelli, V. Dal Santo, A. Trovarelli, M. Boaro, A. Fusi, R. Psaro, S. Recchia, Catal. Today 113 (2006) 81.
[28] D. Tibiletti, A. Goguet, D. Reid, F.C. Meunier, R. Burch, Catal. Today 113 (2006) 94.
[29] F.C. Meunier, D. Tibiletti, A. Goguet, D. Reid, R. Burch, Appl. Catal. A: Gen. 289 (2005) 104.
[30] Y. Yang, C.A. Mims, R.S. Disselkamp, C.H.F. Peden, C.T. Campbell, Top. Catal. 52 (2009) 1440.
[31] V. Dal Santo, L.C. Dossi, A. Fusi, R. Psaro, C. Mondelli, S. Recchia, Talanta 66 (2005) 674.
[32] M.M. Schubert, T.P. Haring, G. Brath, H.A. Gastiger, R.J. Behm, Appl. Spectrosc. 55 (2001) 1537.
[33] C.M. Kalamaras, G.G. Olympiou, A.M. Efstathiou, Catal. Today 138 (2008) 228.
[34] J. Sirita, S. Phanichphant, F.C. Meunier, Anal. Chem. 79 (2007) 3912.
[35] F.C. Meunier, D. Reid, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, W. Deng, M. Flytzani-Stephanopoulos, J. Catal. 247 (2007) 277.
[36] V. Matyshak, O. Krylov, Catal. Today 25 (1995) 1.
[37] J. Couble, P. Gravejat, F. Gaillard, D. Bianchi, Appl. Catal. A: Gen. 371 (2009) 99.
[38] F.C. Meunier, A. Goguet, S. Shekhtman, D. Rooney, H. Daly, Appl. Catal. A: Gen. 340 (2008) 196.
[39] G. Jacobs, B.H. Davis, Appl. Catal. A: Gen. 284 (2005) 31.
[40] F.C. Meunier, D. Tibiletti, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, Catal. Today 126 (2007) 143.
[41] R. Leppelt, B. Schumacher, V. Plzak, M. Kinne, R.J. Behm, J. Catal. 244 (2006) 137.
[42] T. Shido, Y. Iwasawa, J. Catal. 136 (1992) 493.
[43] G. Jacobs, B.H. Davis, Appl. Catal. A: Gen. 333 (2007) 192.
[44] A.A. Gokhale, J.A. Dumesic, M. Mavrikakis, J. Am. Chem. Soc. 130 (4) (2008) 1402.
[45] J.A. Rodriguez, P. Liu, J. Hrbek, J. Evans, M. Perez, Angew. Chem. Int. Ed. 46 (2007) 1329.