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Quantitative DRIFTS investigation of possible reaction mechanisms for the water–gas shift reaction on high-activity Pt- and Au-based catalysts

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Abstract

The present work emphasizes the importance of including a full quantitative analysis when in situ operando methods are used to investigate reaction mechanisms and reaction intermediates. The fact that some surface species exchange at a similar rate to the reaction product during isotopic transients is a necessary but not sufficient criterion for participation as a key reaction intermediate. This is exemplified here in the case of highly active low-temperature water–gas shift (WGS) catalysts based on gold and platinum. Operando DRIFTS data, isotopic exchanges, and DRIFTS calibration curves relating the concentration of formate species to the corresponding DRIFTS band intensity were combined to obtain a quantitative measure of the specific rate of formate decomposition. Despite displaying a rapid isotopic exchange rate (sometimes as fast as that of the reaction product CO_2), the concentration of formates seen by DRIFTS was found to account for at most only 10% of the CO_2 produced under the experimental conditions reported herein. These new results obtained on $Au/CeZrO_4$ and Pt/CeO_2 preparations (which are among the most active low-temperature WGS catalysts reported to date), led to the same conclusions regarding the minor role of IR-observable formates as those obtained in the case of less active $Au/Ce(La)O_2$ and Pt/ZrO_2 catalysts.

Keywords: Operando; In situ; SSITKA; DRIFT; FTIR; Spectroscopy; Water–gas shift; Formate; Surface species; Gold; Ceria; Spectator

1. Introduction

Operando techniques are growing in importance with the realization that ex situ methods can be misleading. We have recently reported that the reactivity of surface species, such as carbonates and formates, adsorbed over redox oxide-based catalysts can dramatically depend on the experimental procedure used [1]. However, although operando techniques can in principle provide evidence about reaction mechanisms and pivotal reaction intermediates, it is important to be aware that the conclusions may be misleading in the absence of a full quantitative analysis of the results. There have been relatively few in situ and operando quantitative investigations of surface species. A few examples can be found especially when characterization techniques were combined: transmission FT-IR and gravimetry [2], gravimetry and temperature-programmed techniques [3], isotopic exchange and laser Raman spectroscopy [4], and UV–vis–NIR and Raman spectroscopies [5].

Diffuse reflectance FT-IR spectroscopy (DRIFTS) is increasingly being used as a means to investigate the reactivity of surface species under reaction conditions, but it is usually considered only a qualitative technique. However, we have 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 [6]) and that a calibration curve relating band intensity to adsorbate concentration is available [7]. We also showed that an appropriately modified DRIFTS cell reactor led to reaction rates identical to those measured in a linear quartz tube plug flow reactor [7].

The combination of DRIFTS or transmission FTIR and steady-state isotopic transient kinetic analysis (SSITKA [8]) is a powerful combination for investigating the reactivity of surface species under reaction conditions. The operando DRIFTS–

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SSITKA method used in the present study relies on using a single catalytic bed, which allows DRIFTS characterization 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 [9–11]. This methodology is similar to that developed earlier for transmission FTIR by Chuang et al. [12,13]. These techniques derived from the so-called "isotopic jump" technique of Tamaru et al. [14], which relied on a two-bed IR cell.

In examples dealing with the water–gas shift (WGS) reaction over Pt/ZrO_2 [15] and Pt/CeO_2 [16], we have shown that the formates adsorbed on the catalysts were exchanged on a significantly longer time scale than that of the reaction product CO_2, clearly stressing that formates were essentially spectators in these cases. However, it was also observed that formates were exchanged on the same time scale as that of CO_2 at higher temperatures over the Pt/CeO_2. The fact that surface species exchange as rapidly as the main reaction product during a SSITKA–DRIFTS experiment cannot yet be taken as unambiguous evidence that these species belong to the main reaction pathway. This was clearly exemplified in our study of the WGS reaction over a catalyst that exhibited a rather low activity (0.6 at% $Au/Ce(La)O_2$ [17]). Despite the fact that formates and CO_2 exchanged on similar time scales, the specific rate of formate decomposition (reported to the catalyst mass) was actually found to be more than an order of magnitude lower than the rate of CO_2 production [7].

In relation to the interest that low-temperature WGS on noble metal-based catalysts has received over the past years and the recurrent debate on the role of formates determined by IR spectroscopy [18–43], here we report new quantitative SSITKA–DRIFTS data showing that the IR-observable formate species are not important in the reaction mechanism for high-activity $Au/CeZrO_4$ [44,45] and Pt/CeO_2 catalysts [16]. Because the SSITKA–DRIFT analysis of the Pt-based material has been reported elsewhere [16,46], only the quantification of the formate concentration and the corresponding decomposition rate calculation are developed here for this sample.

2. Experimental

The experimental setup consisted of an in situ high temperature diffuse reflectance IR cell (from Spectra-Tech) fitted with ZnSe windows. The DRIFTS cell was located in a Bruker Equinox 55 spectrometer operating at a resolution of 4 cm^{-1}. The reactor crucible was modified to ensure plug-flow conditions throughout the catalyst bed. The interface between the ceramic reactor and the metallic base plate was sealed with PTFE tape to prevent any sample bypass. The original porous bed to support the sample was replaced by an inert metallic mesh. The WGS reaction rates measured with this cell were equal to those measured in a conventional tubular plug-flow reactor [7]. No reactant conversion was observed when the crucible was heated up to the reaction temperature in the absence of catalyst.

The catalysts used were a 2 wt% $Au/CeZrO_4$ and a 2 wt% Pt/CeO_2, the details of which have been reported previously [45,46]. The catalyst mass placed in the crucible was 60 ± 3 mg in the case of the $Au/CeZrO_4$ and 115 ± 5 mg in the case of the denser Pt/CeO_2. The purity of the gases used (i.e., H_2, Kr, CO, and Ar, supplied by BOC) was >99.95%. The ^{13}CO was 99% pure (supplied by Cambridge Isotope Laboratories). The DRIFTS cell was connected to the feed gas cylinders through low-volume stainless-steel lines. The gas flows were controlled by Aera mass flow controllers, which were calibrated regularly. A 4-way valve was used to allow rapid switching between two reaction feeds when appropriate. High-purity water was introduced using a single saturator that delivered a constant and accurate water level. Note that the water delivery was completely unaffected by the valve switching (as determined by MS or GC analyses [16]).

Unless stated otherwise, the catalyst was brought up to reaction temperature under Ar, after which water was added to the Ar stream. A reference DRIFTS single scan was recorded after the signal was stabilized. The reaction mixture was subsequently introduced at a total flow rate of 100 ml min^{-1}. The reaction flow was going down the reactor bed; therefore, the upper layer of the catalyst (that mostly probed by the DRIFTS technique) was at the front of the bed.

Steady-state conditions in terms of the concentration of the surface species measured by DRIFTS were reached in less than 30 min. The assignment of the IR bands and the integration method are described in Section 3. The IR data are reported as $\log 1/R$, with $R = I/I_0$, where R is the sample reflectance, I_0 is the intensity measured on the sample after exposure to the CO-free feed, and I is the intensity measured under reaction condition. The pseudo-absorbance $\log 1/R$ gives a better linear representation of the band intensity against sample surface coverage than that given by the Kubelka–Munk function for strongly absorbing media, such as those based on CeO_2 [6].

The calibration standards used to relate the formate DRIFTS signal to the concentration of these species over the catalysts were prepared by incipient wetness impregnation of sodium formate (Aldrich, 99.9%) solutions over the corresponding supports. The samples were dried in ambient air in an oven at 80 °C after impregnation, after which the DRIFTS spectra of the standards were collected under pure Ar at 80 °C. The supports free of noble metals were used to prevent any formate decomposition by the metals during the analysis [1]. The difference in the mid-IR scattering and absorption properties of the materials with and without noble metal was negligible in the present case, as was found previously for SiO_2 and Pt/SiO_2 [6]. Several samples of the same standard were reloaded in the DRIFTS cell, and the measurements were reproducible within ±10%.

3. Results and discussion

The typical in situ DRIFT spectrum obtained during the WGS reaction over the highly active $Au/CeZrO_4$ is shown in Fig. 1. The ^{12}C-spectrum exhibited a band associated with formate species at 2841 cm^{-1} (C–H stretching [47]) and carbonyl at 2097 cm^{-1} (CO adsorbed on Au^0 edge or defect sites [48–50]). The other bands in the 1700–1200 cm^{-1} region were due to formates and carbonates. The support hydroxyl groups also were observed at 3673 cm^{-1} (free hydroxyls) and

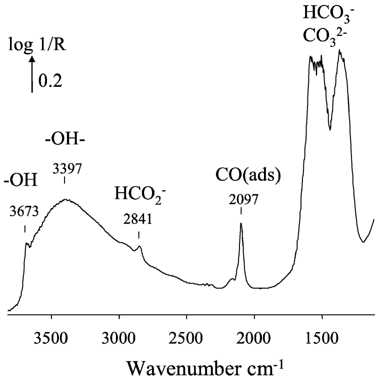

Fig. 1. In situ DRIFT spectrum of the Au/CeZrO$_4$ at steady-state under a stream of 2.5% ^{12}CO + 7% H_2O + 13% H_2 in Ar.

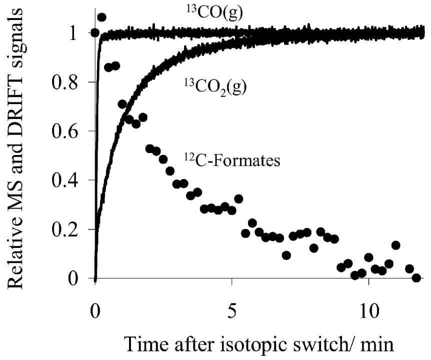

Fig. 2. Comparison of the relative exchange of the gas-phase CO and CO_2 and surface formate species during an isotopic exchange over the Au/CeZrO$_4$. $T = 125\,^{\circ}\mathrm{C}$. Feed: 2.5% ^{13}CO, 7% H_2O, 13% H_2 in Ar. The sample was initially at steady-state under the corresponding non-labeled feed: 2.5% ^{12}CO, 7% H_2O, 13% H_2 in Ar.

3397 cm^{-1} (H-bonded hydroxyls). The in situ spectrum obtained over the Pt/CeO$_2$ material was similar and is described in detail elsewhere [46,47].

Using SSITKA techniques allows us to assess the chemical reactivity of the formate species with respect to the formation of the reaction product CO_2 under reaction conditions. This technique involves replacing one of the reactants (here ^{12}CO) by an isotopomer (here ^{13}CO) during the 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}C- or ^{12}C-containing carbonyl and formates) by DRIFTS. The DRIFTS bands of the surface species typically shift to lower wavenumbers during the analysis, and various integration methods can be used to accurately quantify the surface species exchange (see [7,9,46,47] for the description of the integration methods and typical ^{12}C and ^{13}C spectra obtained over similar catalyst formulations).

The carbonyl exchange (not shown) over these two highly active catalysts was complete in about 0.1 min, which was as fast as that of CO(g) and that of the Kr tracer (not shown), indicating that the exchange time of these species was limited by the purge of the system. In contrast, the exchange times of CO_2 and the formate species over the Au/CeZrO$_4$ were significantly longer than the purge time of the DRIFTS cell (Fig. 2). The longer half-exchange time of formates (ca. 2 min) compared with that of CO_2 (ca. 0.6 min) was a strong indication that formates detected by DRIFTS were not the main reaction intermediates in the formation of CO_2, whereas the rapidly exchanging carbonyl was the potential main intermediate over the Au/CeZrO$_4$.

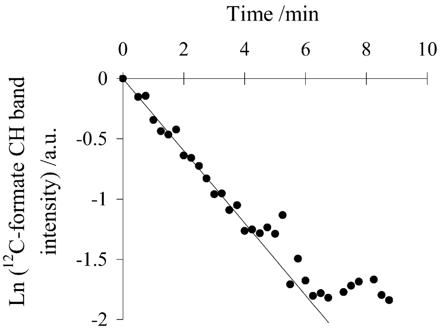

Fig. 3. Logarithm of the relative intensity of the ^{12}C-formate DRIFT band relating to the data reported in Fig. 2.

The comparison of the CO_2 and formate-exchange curves was more intriguing in the case of the Pt/CeO$_2$ material [16]. The formate exchange was significantly slower than that of CO_2 at 160 and 180 °C, suggesting that formates were unimportant reaction intermediates at these temperatures. 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 [16].

The relevance of the formates seen by DRIFTS in this work (Fig. 1) and those in Ref. [16] 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) 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 of formate decomposition, denoted as k [7],

$$\text{rate of formate decomposition} = k[\text{formate}].$$

The value of k was obtained during a ^{12}CO–^{13}CO isotopic exchange under WGS conditions by measuring the slope of the line representing the logarithm of the formate concentration as a function of time following the isotopic switch (see Fig. 3 for Au/CeZrO$_4$ at 125 °C and Ref. [16] for Pt/CeO$_2$).

Calibration curves (Fig. 4) were also drawn to accurately quantify the concentration of formates. The calibration curves were obtained by measuring the intensity of the CH stretching DRIFTS band centered at around 2841 cm^{-1} of standard samples. Exemplar in situ spectra measured over the Au and Pt ceria-based catalysts and spectra of the calibration standards are shown in Fig. 5. The integration ranges were 2890–2800 cm^{-1} for the Au/CeZrO$_4$ and 2880–2800 cm^{-1} for the Pt/CeO$_2$. The calibration curves provide a simple and quantitative measure of the amount of surface formates produced at steady state under reaction conditions. It is important to note that the slope of the calibration curve was different for each catalyst, stressing that each calibration curve is material-dependent and cannot be extrapolated to other catalysts. This observation results from the fact that the sample scattering and absorptiv-

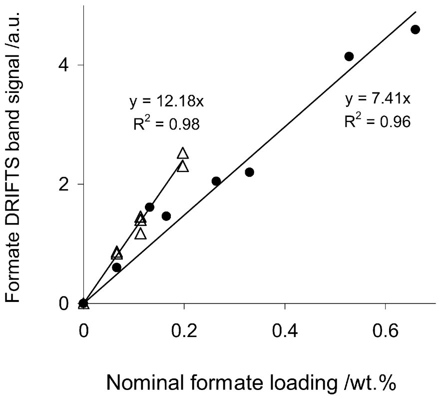

Fig. 4. Calibration plots relating the area of the formate CH stretching DRIFT band to the nominal formate loading on the (▲) $CeZrO_4$ and (●) CeO_2 supports impregnated with sodium formate.

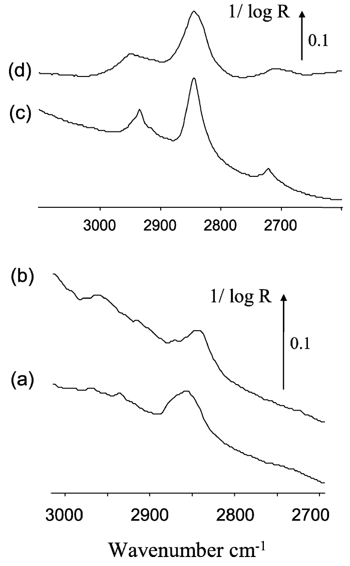

Fig. 5. (a) DRIFT spectrum recorded at 80 °C in Ar over $CeZrO_4$ impregnated with 0.11 wt% of formate ions and (b) in situ DRIFT spectrum recorded over $Au/CeZrO_4$ under 2.5% CO, 7% H_2O, 13% H_2 in Ar at 125 °C. (c) DRIFT spectrum recorded at 80 °C in Ar over CeO_2 impregnated with 0.67 wt% formate ions and (d) in situ DRIFT spectrum recorded over Pt/CeO_2 under 2% CO + 7% H_2O in Ar at 160 °C.

ity will depend to a great degree on its composition, texture, and porosity. Because calibration curves relating to DRIFTS analyses are also known to show nonlinear behavior [51], it is important to not extrapolate outside the range of standards measured.

The decomposition rate of the formate species yielded the upper limit of the rate of formate decomposition to CO_2, because it is likely that formates were not only decomposing to give CO_2, but instead gave a mixture of CO and CO_2 [24]. Even assuming that formates decomposed solely to CO_2, the rate of formate decomposition for our highly active $Au/CeZrO_4$ and Pt/CeO_2 WGS catalysts accounted for less than 5% and 10% of the total rate of CO_2 formation in the range of temperatures and experimental conditions used here, respectively (Fig. 6). Therefore, the formates detected by DRIFTS are minor reaction intermediates even with these very active catalysts.

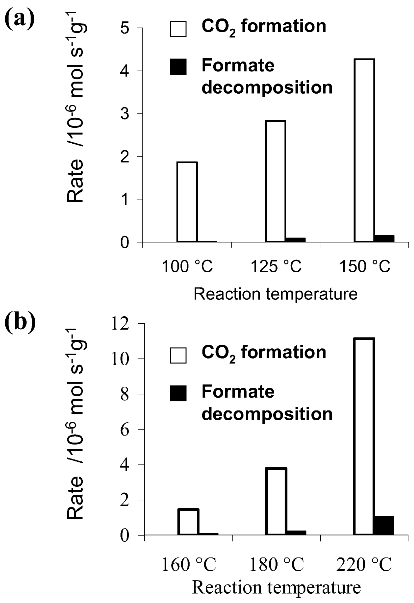

Fig. 6. (a) Rate of CO_2 production and rate of formate decomposition over the $Au/CeZrO_4$ at three different temperatures under 2.5% CO, 7% H_2O, 13% H_2 in Ar. (b) Rate of CO_2 production and rate of formate decomposition over the Pt/CeO_2 at three different temperatures under 2% CO + 7% H_2O in Ar.

The experimental conditions used here are similar to those used in most other papers reported so far. However, it should be stressed that Davis and co-workers, who proposed that the formates seen by IR were main reaction intermediates, typically used much higher concentrations of water (up to 89% [40]). A higher partial pressure of water could accelerate formate decomposition significantly; therefore, a full quantitative analysis under the conditions used by Davis et al. would be necessary to determine the relevance of the formates detected by DRIFTS in this case.

Our work does not allow us to determine the exact nature of the main reaction intermediates. It is possible that the main reaction intermediates (not excluding some highly reactive hypothetical formates) have very low steady-state surface concentrations and are not observable by IR. Recent theoretical work on Au/CeO_2 has suggested that an associative mechanism involving a carboxyl species HOCO* (rather than a formate HCOO**) occurs [52,53], although the synergistic role of the support (possibly involved in the activation of water) remains incompletely understood.

The unambiguous conclusions obtained here on the minority role of formates detected by IR do not contradict a statement from our earlier paper [16] regarding the Pt/CeO_2 catalysts suggesting that the formates seen by DRIFTS are only potential main reaction intermediates at the higher temperatures. The positive conclusions reported here supercede the nonconclusive statements reported previously [16], stressing yet again that nonfully quantitative work is merely speculative.

4. Conclusion

The formates seen on DRIFTS are not part of the major reaction pathway leading to CO_2 over our highly active $Au/CeZrO_4$

and Pt/CeO_2 WGS catalysts under the experimental conditions used in the present work. The proportion of CO_2 formed by a route involving the formates seen by DRIFTS is $<5\%$ for the Au/$CeZrO_4$ and $<10\%$ for the Pt/CeO_2. This work further demonstrates that with careful experimentation, it is possible to perform fully quantitative operando DRIFTS, and that unambiguous conclusions can be drawn from these data.

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