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On the complexity of the water-gas shift reaction mechanism over a Pt/CeO_2 catalyst: Effect of the temperature on the reactivity of formate surface species studied by operando DRIFT during isotopic transient at chemical steady-state

F.C. Meunier *, D. Tibiletti, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch

CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG Northern Ireland, United Kingdom

Abstract

The present report investigates the role of formate species as potential reaction intermediates for the WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$) over a Pt-$CeO_2$ catalyst. A combination of operando techniques, i.e., in situ diffuse reflectance FT-IR (DRIFT) spectroscopy and mass spectrometry (MS) during steady-state isotopic transient kinetic analysis (SSITKA), was used to relate the exchange of the reaction product CO_2 to that of surface formate species. The data presented here suggest that a switchover from a non-formate to a formate-based mechanism could take place over a very narrow temperature range (as low as 60 K) over our Pt-CeO_2 catalyst. This observation clearly stresses the need to avoid extrapolating conclusions to the case of results obtained under even slightly different experimental conditions. The occurrence of a low-temperature mechanism, possibly redox or Mars van Krevelen-like, that deactivates above 473 K because of ceria over-reduction is suggested as a possible explanation for the switchover, similarly to the case of the CO–NO reaction over Cu, Pd and Rh–CeZrOx (see Kaspar and co-workers [1–3]).

Keywords: Formate; DRIFTS; FTIR; Operando; In situ; Spectroscopy; Water-gas shift; Reaction intermediate; Spectator; SSITKA; Deactivation; Ceria

1. Introduction

The water-gas shift reaction (WGS, $CO + H_2O \rightarrow CO_2 + H_2$) is of importance for the low-temperature production of CO-free H_2 to be used for PEM fuel cells. Recent studies have shown that noble metals (e.g., Pt, Au) supported on CeO_2 are promising low-temperature WGS catalysts [4–6]. Similarly to the case of Cu and magnetite-based catalysts [7–11], two main types of reaction mechanism have been proposed. First, a redox (i.e., regenerative) route has been suggested, in which CO adsorbs on a Pt site and is oxidised by oxygen atoms from the ceria with re-oxidation of the ceria occurring by reaction with H_2O [4,12,13]. A second non-redox mechanism (i.e., associative) has also been proposed, in which the main reaction intermediate is a surface formate species [14,15]. In a more general perspective, formates have also been proposed as a surface intermediate during reaction between CO_2 and H_2 for the reverse WGS reaction (RWGS) and methanol synthesis over Pt [16,17] or Cu-based materials [18,19].

Our laboratory has recently reported [20] a detailed study of the reaction mechanism of the RWGS reaction (RWGS, $CO_2 + H_2 \rightarrow CO + H_2O$) over a Pt-$CeO_2$ material, using a new combination of operando techniques [21,22], i.e., in situ diffuse reflectance FT-IR (DRIFT) spectroscopy and mass spectrometry (MS) during steady-state isotopic transient kinetic analysis (SSITKA [23–26]). The combination of FTIR in the transmission mode and SSITKA analysis had been successfully introduced by Tamaru and co-workers in the 1970s, named as ‘‘isotopic jump’’ method [27]. However, these authors often used a large catalyst wafer off the IR beam pathway, in addition to the minute amount of sample making the thin IR-studied wafer, to be able to achieve meaningful conversions. Therefore, the IR signal and reactant conversion related to two spatially different locations in this two-bed configuration [27]. Chuang and co-workers have since reported many informative studies on transmission–FT-IR and SSITKA regarding for instance CO

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* Corresponding author. Tel.: +44 28 90 974420; fax: +44 28 90 382117.
E-mail address: f.meunier@qub.ac.uk (F.C. Meunier).

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methanation, using a single bed system [28,29]. We have recently extended this method to the case of diffuse reflectance FT-IR [20], as there are some intrinsic advantages in using DRIFT, such as a better mimicking of real plug-flow reactors and directly using powders instead of wafers compacted at high-pressure. However, it is crucial that the DRIFT cell is appropriately tested to ensure that no bed by-pass takes place and that the bed area is not a dead-zone (see Section 2).

As far as the RWGS is concerned, earlier work had shown that non-operando experiments could lead to misleading conclusions as far as the true reactivity (i.e., at steady-state under reaction condition) of carbonate and formate species were concerned [30,31]. Our combined techniques (DRIFT + MS + SSITKA) enabled us to discriminate between potential main reaction intermediates and spectator species, and in the conditions used there, we unambiguously showed that formates were spectator species [20].

The present short report aims at investigating the role of formate species for the WGS reaction over a Pt-CeO_2 material. On the one hand, we should expect formate to be spectator species, based on our earlier RWGS study and the micro-reversibility principle [32]. Yet, one should bear in mind that the structure of the catalyst itself is likely to be modified depending on the reaction feed, since ceria partly reduces under reaction conditions [17] and that WGS and RWGS feeds are expected to have a different oxidising/reducing power [30,33]. On the other hand, the vast amount of data reported by Jacobs et al. [15–17] and Iwasawa and co-worker [14] all tend to favour a role as main reaction intermediate for formates, in particular for feeds with high H_2O/CO ratio [15–17]. The data presented here will show that a switchover from a non-formate to a formate-based mechanism could take place over a very narrow temperature range over a given Pt-CeO_2 catalyst.

2. Experimental

The catalyst used in this study was a 2% Pt/CeO_2 prepared using homogeneous precipitation of Pt(II) DNDA (Johnson Matthey) in urea with aqueous ammonia, in manner similar to that given in reference [34]. The BET surface area of the sample was 135 $m^2\ g^{-1}$. The purity of the gas supplied by BOC (Kr, CO, O_2, Ar) was higher than 99.95%. High purity water was introduced using one saturator, which delivered a constant and accurate level of water. The ^{13}CO was 99% pure (supplied by Cambridge Isotope Laboratories). The cell was connected to the feed gas cylinders through low volume stainless-steel lines. The gas flows were controlled by Aera mass flow controllers. A 4-way valve was used to allow a fast switching between two reaction feeds, when appropriate.

The DRIFTS (from Spectra-Tech®) cell was located in a Bruker Equinox 55 spectrometer, operating at a resolution of 4 cm^{-1}. The reactor of the DRIFT cell was modified to ensure that no catalyst bed by-pass took place, contrary to the case of the as-received cell. The original crucible was replaced by a hollow ceramic to decrease the reactor pressure drop, while the gap between the ceramic and the metal base support was sealed with Teflon. An inert grid was used to support the catalyst. The original cell only allowed a partial conversion (i.e., ca. 20%) of CO over a Pt/SiO_2 in the presence of excess oxygen between 473 and 600 K, while total conversion in CO oxidation could be obtained at 473 K using the modified cell. The system average residence time, which was measured during a step change between a mixture of Ar + Kr to pure Ar, was ca. 6 s. The outlet of the DRIFT cell was connected to a quadrupole mass spectrometer (Hiden). The mass spectrometer was equipped with a capillary inlet system with bypass allowing fast response (i.e., 100 ms) for the sampling. Both feed lines were connected to an ultra-low differential pressure transducer (Honeywell 395-257) and a high precision metering valve (Nupro) in order to control and tune the pressure of both feed lines.

The amount of 2% Pt/CeO_2 catalyst used was 80 ± 5 mg (particle diameter <150 μm). Prior to measurement, the sample was reduced in situ for 1 h at 573 K in a 50% H_2/Ar mixture at a total flow of 40 ml min^{-1}. After the reduction step, the cell was purged with Ar and the temperature of the reactor was set to the desired value. The reaction mixture, i.e., 2% ^{12}CO + 7% H_2O in Ar, was then introduced at a total flow rate of 100 ml min^{-1} (GHSV = ca. 21,000 h^{-1}). The concentration of surface species measured by DRIFTS all reached a constant value in less than 30 min. After at least 1 h, the unlabelled gas feed was replaced with a 2% ^{13}CO + 7% H_2O + 2% Kr mixture in Ar, the Kr being used as an inert tracer. Spectra were recorded at regular intervals (typically every 10 s) for at least 30 min following the isotopic switch. The IR region used for the quantification of the concentration of the ^{12}C-containing formates was: 3000–2950 cm^{-1} (single-point baseline at 3050 cm^{-1}). The description of the IR spectra and integration method has been reported in details elsewhere [31]. The ^{12}C and ^{13}C-responses both in the case of the formate species and that of the CO_2 were symmetric, so any set of exchange curves could be used to compare the relative rate of exchange.

3. Results and discussion

The utilisation of the SSITKA techniques requires that the switches between feeds are as fast and smooth as possible, along with keeping the concentration of each reactant unchanged (except for that of the molecule to exchange). The pressure drop over the lines was carefully balanced before reaction, and the data reported in Figs. 1 and 2 give an indication of the stability of the water and CO delivery during switches over our setup. The water and CO concentration were totally unaffected by the valve switching (the MS signals were normalised to that of the Kr tracer when required). For the sake on conciseness, the DRIFT spectra collected are not shown, but those are essentially identical to the spectra reported in an earlier study over a similar catalyst [31].

The relative variation of the intensity of the ^{12}C-containing formate IR band during an isotopic switch from the ^{12}C to ^{13}C-containing feed (i.e., $^{12}CO + H_2O$ replaced with $^{13}CO + H_2O$) is shown at two different temperatures: 433 K (Fig. 3a) and 493 K (Fig. 3b). The exchange was faster at the higher temperature, i.e., the time required to obtain 50% exchange was about 15 min at 433 K (Fig. 3a) and ca. 1 min at 493 K

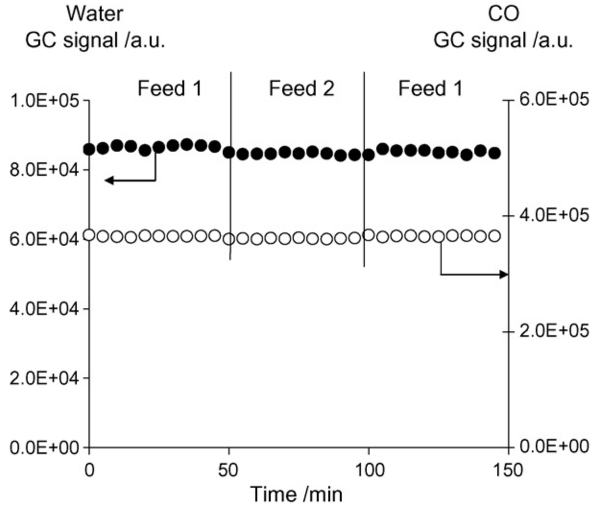

Fig. 1. (●) Water (measured by GC-TCD) and (○) CO (measured by GC-FID-Methanator) signals with time on stream. The vertical lines indicate when the 4-way valve was switched between two identical gas feeds. Feed: 2% CO + 7% H_2O, Ar diluent.

(Fig. 3b). The signal decay fitted in both cases a single exponential curve, i.e., the corresponding semi-log plots yielded straight lines (Fig. 4). This data suggest that the exchange of the formate species most likely followed a first-order law, i.e.,

$$\frac{d[\text{formate}]}{dt} = -k[\text{formate}]$$

with a single rate constant k at each temperature (Note that the apparent rate constant k may contain a contribution from the surface coverage of other surface intermediates or/and reactant pressures). Therefore, it is reasonable to propose that all the formates species as seen by IR spectroscopy in the present work were of the same reactivity. (Note that surface formates with different reactivity have been observed over a Au–La–CeO_2 sample [35]. In this case, the formate exchange curve could be exactly decomposed into the sum of two exponential terms of similar amplitudes, assigned to so-called ‘‘slow’’ and ‘‘fast’’ formates.)

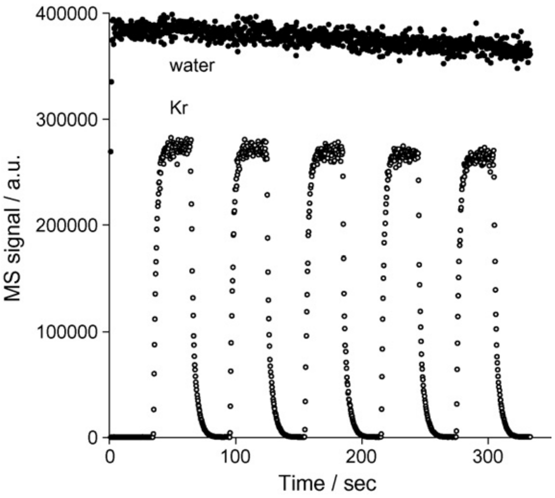

Fig. 2. (●) Water and (○) Kr signals as measured by MS with time on stream during a series of switches of the 4-way valve allowing alternating gas feeds (H_2O + CO + Ar ↔ H_2O + CO + Ar + Kr). Feed: 2% CO + 7% H_2O + 2% Kr (if any), Ar diluent.

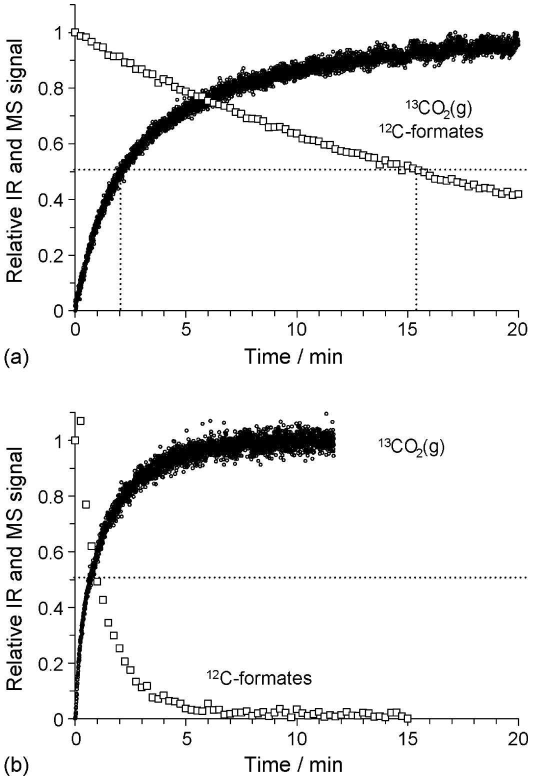

Fig. 3. Relative intensity of $^{13}CO_2$(g) (●) and of ^{12}C-containing surface formate species (□) following a ^{12}CO–^{13}CO isotopic switch under steady-state WGS conditions over a 2% Pt/CeO_2 at (a) 433 K and (b) 493 K. Feed: 2% ^{13}CO + 7% H_2O in 2% Kr/Ar.

The corresponding isotopic exchange of the gaseous reaction product $^{13}CO_2$ were measured recording the signal at mass/z = 45 with the mass spectrometer. A 50% exchange of the reaction product CO_2(g) was achieved in ca. 2 min at 433 K (Fig. 3a) and in ca. 55 s at 493 K (Fig. 3b). The MS signal of the Kr tracer (not shown) dropped to zero in ca. 6 s following the switch, indicating that the flow dynamics of the system were

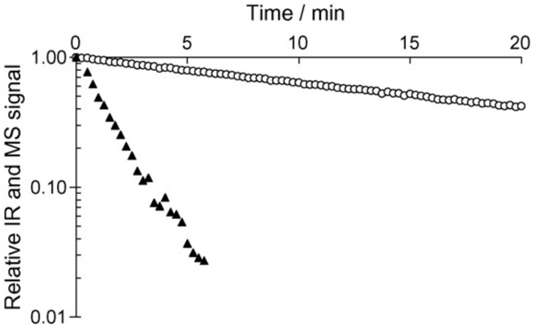

Fig. 4. Semi-log plot of the relative intensity of the IR signal of ^{12}C-containing formate species following a ^{12}CO–^{13}CO isotopic switch under steady-state WGS conditions over a 2% Pt/CeO_2 at 433 K (○) and 493 K (▲). Feed: 2% ^{13}CO + 7% H_2O in 2% Kr/Ar.

fast as compared to that of the exchange processes of interest here.

These data clearly show that at 433 K (Fig. 3a) the isotopic exchange of the surface formates was significantly slower than that of the reaction product CO_2(g). After 2 min following the isotopic switch, 50% exchange of the CO_2(g) was completed, while only ca. 10% of the surface formates were replaced with the corresponding ^{13}C-containing species. Therefore, the main reaction pathway at the lower temperature (433 K) did not involve the formate species seen by DRIFT. These formates were therefore reaction spectators, or most precisely, ‘‘minor’’ reaction intermediates as those eventually decomposed to yield, most likely in part, CO_2. At this temperature, the formates seen by DRIFT belonged to a secondary (slow) reaction pathway, which is not the main reaction route under these conditions.

The situation at 493 K (Fig. 3b) was quite different. The 50% exchange time for both CO_2(g) and the surface formates were essentially identical, indicating that formates seen by DRIFT could possibly be a main surface intermediate in the formation of CO_2(g), as proposed by Jacobs et al. [15–17] over similar materials. Yet, it is worth noting that both species having the same half-exchange time is a necessary but not sufficient condition for formates being main reaction intermediates. In this particular case, we have some evidence (*to be published*) of a significant readsorption of the reaction product CO_2, over the basic ceria [36], requiring a more detailed analysis of the exchange curves [37].

A universal mechanism for the water-gas shift reaction has been proposed by Burch in a recent paper [38], in which it is stressed that the dominant surface intermediate can be a function of reaction conditions. For example, as the temperature is increased the dominant surface species may change from a carbonate or carboxylate species, to a formate species and eventually at high temperatures to a mechanism that is characteristic of a redox process. Similar changes in the dominant intermediate can be expected with changes in the gas composition; all depending on the relative rates of surface species formation and consumption.

Interestingly, the data reported here show that there is a mechanism (i.e., the main route at 433 K) that does not yet involve the formates seen by IR at the lower temperatures. Note that formates have also been shown to be mostly spectator species over Pt-ZrO_2 under similar reaction conditions [39]. The only IR-observable species that seemed to have a kinetic of exchange comparable to that of carbon dioxide at 433 K was the carbonyl species. It is however impossible to accurately quantify the carbonyl exchange [see discussion section on carbonyls reported elsewhere [31]). The nature of the WGS mechanism taking place at 433 K is yet unclear, and it could possibly involve a very low concentration (hence IR-invisible) surface complex (including formates and carbonates/carboxylates). However, a redox or Mars van Krevelen-type mechanism [4,12,13], as also proposed for the preferential oxidation of CO [40], cannot be excluded. Interestingly, Kaspar and co-workers [1–3] suggested the presence of a low-temperature redox reaction pathway in the case of the CO–NO reaction over Cu, Pd and Rh–CeZrOx, and this mechanism was deactivated above 473 K because of the difficulty to re-oxidise ceria at higher temperature.

An extensive surface reduction of ceria to Ce^{III} leading to the formation of stable compounds (in particular carbonates [31] or hydroxycarbonates [41]) appears to be a major reason for CeO_2-based-catalyst deactivation during the WGS reaction [31,33,41–46]. The addition of low concentrations of O_2 to the feed [47] and of zirconia to the catalyst [46] has been successfully employed to increase the oxygen supply and mobility to facilitate ceria re-oxidation. Therefore, the possibility that (1) the main WGS mechanism taking place at 433 K (whether is it truly redox or involves short-lived surface complexes) deactivates at around 473 K and (2) is replaced at higher temperature by a different mechanism based on formates (as detected by DRIFT at 493 K) is a possibility worth considering and is certainly consistent with the data reported here. Eventually, a redox-like mechanism would be ‘‘apparently’’ observed at the higher temperatures (e.g., >600 K [48]), where steady-state surface coverages of adsorbates are low.

In summary, it has been shown that over quite a narrow temperature range, the importance of a surface species can be dramatically different, with formates changing from being essentially spectators to being possible reaction intermediates. Therefore, caution is required when attempting to generalise on the reaction mechanism based on data using different reaction mixtures or reaction temperatures, or even differently prepared catalysts having the same nominal composition.

4. Conclusions

A small change in the reaction temperature can dramatically modify the reactivity of surface formates over a 2 wt.% Pt/CeO_2 catalyst during the water-gas shift reaction. In the present case, the data clearly showed that the formates as seen by DRIFT were essentially spectator species at 433 K, while formates were possible main reaction intermediates at 493 K. The results show that great care is needed when trying to develop a single model for this reaction for a range of catalysts tested using various reaction mixtures at different temperatures. Ceria over-reduction at increased reaction temperatures and the related formation of stable Ce^{III} compounds has been proposed as a possible explanation for the presence of a switchover between different reaction mechanisms at around 473 K.

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