

On the importance of steady-state isotopic techniques for the investigation of the mechanism of the reverse water-gas-shift reaction†

Daniele Tibiletti, Alexandre Goguet, Frederic C. Meunier,* John P. Breen and Robbie Burch
 CenTACat, School of Chemistry, Queen's University Belfast, Belfast, Northern Ireland BT41 1PB.
 E-mail: f.meunier@qub.ac.uk; Fax: +44 28 9097 2117; Tel: +44 28 90974420

Received (in Cambridge, UK) 5th March 2004, Accepted 14th May 2004
 First published as an Advance Article on the web 8th June 2004

The formation and reactivity of surface intermediates in the reverse water-gas-shift reaction on a Pt/CeO₂ catalyst are critically dependent on the reaction conditions so that conclusions regarding the reaction mechanism cannot be inferred using *ex operando* conditions.

Hydrogen fuel cells require hydrogen that contains very low concentrations of carbon monoxide. One important process for reducing the amount of carbon monoxide is the water-gas-shift (WGS) reaction.^{1–7} (eqn. (1)).



Recent studies have shown that noble metals supported on redox oxides such as CeO₂ are promising low-temperature catalysts for the WGS reaction.^{2–7} Two main types of reaction mechanism have been proposed regarding this reaction. A redox mechanism has been suggested, mostly on the basis of kinetic measurements.^{4,6,8} In this mechanism, CO adsorbs on a Pt site and is oxidised by oxygen atoms from the ceria. The support is subsequently re-oxidised by water. Alternatively, a non-redox mechanism has also been proposed, in which the main reaction intermediate is a surface formate species.^{3,9} The conclusions of these studies were partly based on the observation by FT-IR spectroscopy of the surface species typically obtained under WGS reaction conditions and the decomposition/reactivity of these species in vacuum³ or atypical feed gases.^{3,8,9}

The data reported in the present paper deal with the reactivity of the surface species formed under reverse water gas shift (RWGS) conditions (*i.e.*, feed of CO₂ and H₂), for which similar surface reactions as those occurring during the WGS can be expected, based on the principle of microscopic reversibility. A key observation is the sensitivity of the key intermediates to changes in the reaction conditions, and the consequent risk of arriving at an incorrect mechanism. An experiment in which the RWGS reaction intermediates are allowed to accumulate on the catalyst surface and then react or decompose in an **inert atmosphere**, leads to the conclusion that formates are the most reactive species. However, when the reaction intermediates are allowed to react or decompose under steady-state conditions (studied by isotopic switching techniques) it is found that carbonyl and carbonate species are the most reactive surface compounds. The implications of these observations are discussed with respect to the various reaction mechanisms that have been proposed for these reactions.

The experimental details are available on-line as Electronic Supplementary Information†. The main features of the steady-state *in situ* DRIFTS spectrum obtained after 1h under the RWGS feed are shown in Fig. 1(a). Three wavenumber regions were selected, as each of these were unequivocally related to only one type of surface species. The assignment of the IR bands has already been discussed in detail in the literature. The bands at 2947 and 2841 cm⁻¹ are associated with the C–H Fermi resonance doublet of a bidentate formate species located on the ceria. The complex band structure between 2100 and 1900 cm⁻¹ is related to Pt-bound carbonyl species.^{3,10,11} The high-frequency side of the band (centred around 2070 cm⁻¹) is associated with linearly bound CO, probably on a

distribution of heterogeneous adsorption sites (*vide infra*), whereas the lower frequency side of the band may be related to bridged carbonyl species. The bands in the 900–800 cm⁻¹ region are associated with the out-of-plane vibration of carbonate species. At least two carbonate bands were observed (*i.e.*, non-resolved bands at 866 and 851 cm⁻¹), related to different adsorption sites (probably mostly on the support) and/or bonding mode to the surface.

A low-volume 4-way valve allowed a fast switching between the RWGS feed and either an inert purge gas (Ar) or the corresponding isotopically labelled feed (containing ¹³CO₂ instead of ¹²CO₂). After steady-state conditions were reached under the initial RWGS feed, the *in situ* DRIFTS spectrum was recorded every 10 s following the gas switch.

The evolution with time under Ar of the IR band intensity of the various surface species is reported in Fig. 2 (the IR spectra are not shown). The intensity of each band was normalised to that measured before the switch. To remain consistent with the way the intensity of the IR bands were quantified in the case of the isotopic switch (*vide infra*), only the high-frequency side of the bands were integrated, *i.e.*, 2954–2944 cm⁻¹ for the formates (the baseline value was taken at 3050 cm⁻¹), 2110–2050 cm⁻¹ for the carbonyls (the baseline value was taken at 2150 cm⁻¹) and 900–865 cm⁻¹ for the carbonates (the baseline value was taken at 795 cm⁻¹).

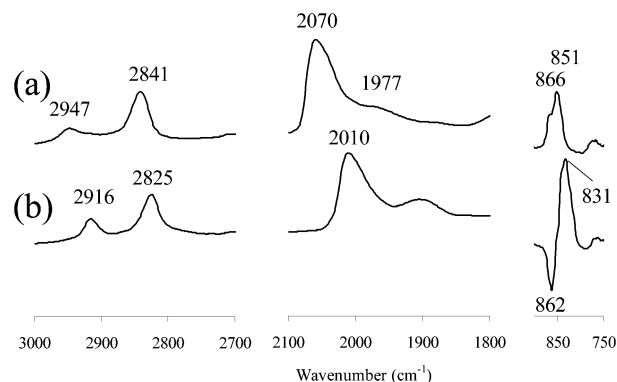


Fig. 1 *In situ* DRIFT spectra of the surface species formed over a 2% Pt/CeO₂ catalyst at 498 K (a) at steady state in 1% ¹²CO₂ + 4% H₂ in Ar and (b) after 90 additional minutes under 1% ¹³CO₂ + 4% H₂ in Ar.

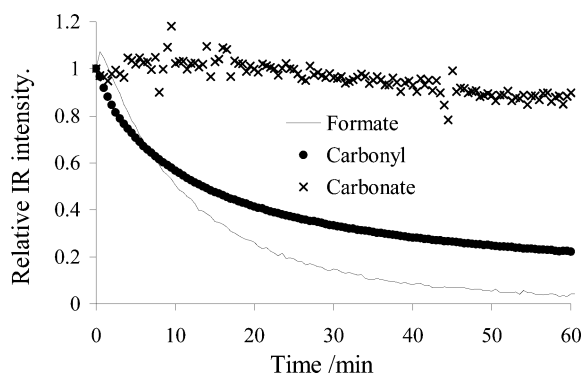


Fig. 2 Relative intensity of the IR bands of the formate, carbonyl and carbonate species as a function of time on stream in Ar. *T* = 498 K.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b4/b403438d/>

When switching to Ar, the intensity of the formate band rapidly decreased to zero, in agreement with earlier data.^{3,9} A 50% loss in signal intensity was observed after *ca.* 10 min (Fig. 2). The 2070 cm^{-1} carbonyl peak decreased in intensity and red-shifted (maximum at 2043 cm^{-1} after 2 hours in Ar), while the low-frequency feature at 1977 cm^{-1} was essentially unchanged (IR data not shown). The gradual shift of the CO band between 2070 and 2043 cm^{-1} suggested the presence of a distribution of heterogeneous adsorption sites (as can be expected over supported noble metal particles), and possibly the occurrence of dipole–dipole (*i.e.*, lateral) interactions at high platinum surface coverage.¹² The carbonyl signal initially decreased at a similar rate as that of the formates (Fig. 2), but a significant fraction of these species was still present after one hour. The intensity of the carbonate band at 851 cm^{-1} slightly decreased, while that at 866 cm^{-1} slightly increased (IR data not shown). Overall, the total intensity of these carbonate bands remained essentially constant with time, probably indicating that a small fraction of the species associated with the 851 cm^{-1} band was quantitatively being converted to that at 866 cm^{-1} . The stability of carbonates on Rh/CeO₂ catalyst initially exposed to a WGS feed and then evacuated in inert gas has also been reported by Hilaire *et al.*⁸

The evolution of the IR band intensity of the ¹²C-containing surface species with time after switching to the isotopically labelled feed (*i.e.*, 1% ¹³CO₂ + 4% H₂ in Ar) is reported in Fig. 3. The IR spectrum obtained at steady-state after 90 min under the labelled feed is shown in Fig. 1(b). The IR bands of all the species of interest exhibited a red-shift, related to the higher mass of the ¹³C isotope. However, the shift in frequency was not sufficient to allow a complete resolution of the ¹²C and ¹³C-IR bands and, therefore, the integration of the intensity of the ¹²C-bands had to be limited to the high-frequency part of the band where there was no contribution from the ¹³C-species. The changes in the intensity of the IR bands of the ¹²C-containing surface species during the isotopic exchange was dramatically different from that obtained in the presence of the inert purge gas. A complete exchange of both the carbonyl and carbonate species could be obtained in less than 10 min., that is, faster than the exchange time of the formates. The negative band observed at 862 cm^{-1} (Fig. 1b) indicates that some of the carbonate species that were present on the sample after the pre-reduction were readily exchanged in RWGS conditions. It is also surprising to note that the rate of isotopic exchange of the formates was slower than that of desorption/decomposition of these same species under Ar

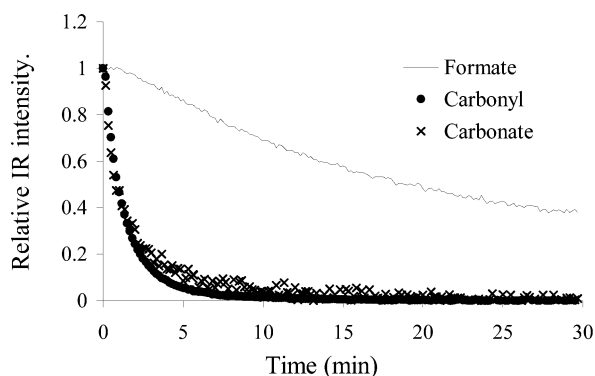


Fig. 3 Relative intensity of the IR bands of the ¹²C-containing formate, carbonyl and carbonate species as a function of time on RWGS stream containing ¹³CO₂. *T* = 498 K.

(*i.e.*, time for 50% exchange and desorption/decomposition: 20 and 10 min, respectively).

Our data clearly show that *in operando* studies¹³ are necessary in order to investigate the true reactivity pattern of surface species during the RWGS over noble metal-promoted ceria. For example, formates are identified as the most reactive surface intermediates under an inert gas, but they exchanged significantly slower than other surface species under true reaction conditions in the isotopic exchange experiment. The difference in the reactivity of the carbonates was also striking between the two sets of conditions reported here. Other experiments have shown that the carbonate species are readily desorbed following the addition of O₂ to the inert purge gas (in agreement with earlier data⁸). This suggests that one of the main origins for the difference in the reactivity of surface species with respect to the reaction feed may be related to the average oxidation state of the ceria. With respect to this point, while our reaction feed (*i.e.*, 1% CO₂ + 4% H₂) was globally reducing, the actual steady-state oxidation state of the ceria under RWGS conditions will depend on the relative rate of reduction by H₂ (and the CO formed) and on oxidation by CO₂ (and the water formed). These observations emphasise the fact that different experimental conditions affect the oxidation state of ceria and, as a consequence, the likelihood of a redox or a non-redox (*e.g.*, formate-based) reaction mechanism will change.

It is likely that the reactivity of similar RWGS or WGS catalysts will also depend on the reaction conditions and so conclusions on the reactivity of surface intermediates derived *ex operando* need to be treated with caution. In the present RWGS case over our Pt/Ceria sample, the kinetic data (*to be published elsewhere*) show that the isotopic exchange time of CO(g) was identical to that of carbonates and carbonyl species, stressing that formates are spectator species.

The authors gratefully acknowledge the financial support of Johnson Matthey Plc. The CONCORDE Concerted Action on nanostructured oxides (NMP2-CT-2004-505834) is also acknowledged for financial support.

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