

On the complexity of the water-gas shift reaction mechanism over a Pt/CeO₂ catalyst: Effect of the temperature on the reactivity of formate surface species studied by operando DRIFT during isotopic transient at chemical steady-state

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Abstract

The present report investigates the role of formate species as potential reaction intermediates for the WGS reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) over a Pt-CeO₂ 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 CO₂ 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-CeO₂ 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]).

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1. Introduction

The water-gas shift reaction (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is of importance for the low-temperature production of CO-free H₂ to be used for PEM fuel cells. Recent studies have shown that noble metals (e.g., Pt, Au) supported on CeO₂ 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 H₂O [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 CO₂ and H₂ 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, $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) over a Pt-CeO₂ 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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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-CeO₂ 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 H₂O/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-CeO₂ catalyst.

2. Experimental

The catalyst used in this study was a 2% Pt/CeO₂ 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 m² g⁻¹. The purity of the gas supplied by BOC (Kr, CO, O₂, Ar) was higher than 99.95%. High purity water was introduced using one saturator, which delivered a constant and accurate level of water. The ¹³CO 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/SiO₂ 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/CeO₂ 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% H₂/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% ¹²CO + 7% H₂O 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% ¹³CO + 7% H₂O + 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 ¹²C-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 ¹²C and ¹³C-responses both in the case of the formate species and that of the CO₂ 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 ¹²C-containing formate IR band during an isotopic switch from the ¹²C to ¹³C-containing feed (i.e., ¹²CO + H₂O replaced with ¹³CO + H₂O) 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

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