

Review

A critical analysis of the experimental evidence for and against a formate mechanism for high activity water-gas shift catalysts

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ABSTRACT

An in-depth analysis of the evidence for and against a formate-based mechanism for the water-gas shift reaction has shown that with very few exceptions the published results cannot be used to provide any mechanistic information either for or against a formate model. Where reliable quantitative data are available, these show unequivocally that for all high activity catalysts the contribution of IR-observable formate to the production of CO₂ is only of minor importance. It is found that the formates seen by IR typically account for less than about 10–15% of the total WGS reaction products. The formates observed by IR were potentially the main reaction intermediates only in the case of very low activity catalysts. For the high activity catalysts that are of interest for current fuel cell applications it is clear that the major contribution of a formate mechanism is yet to be proven. The current published in situ/operando FTIR data relating to formates cannot be used to elucidate the main reaction mechanism nor for deriving improved catalytic formulations.

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1. Introduction

Investigating the mechanism of any catalytic reaction involves the interpretation of experimental results and also in more recent times the interpretation of density functional theory calculations. The challenge in reliably interpreting such experimental or theoretical information can lead to widely different conclusions. The purpose of this paper is to assess the evidence for and against

a specific reaction mechanism, namely the “formate” mechanism, for the water-gas shift reaction (WGS: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$). However, the process set out for the analysis of the WGS reaction mechanism can be applied to many other investigations of catalytic reaction mechanisms in which there has been an over-interpretation of experimental or theoretical results when there is no quantitative basis on which to arrive at the stated conclusions.

In addressing the issues raised in the published literature on the mechanism of the WGS reaction we should be mindful of the words of Confucius on the meaning of wisdom:

“To accept that what is known is known and to accept that what is not known is not known, that is wisdom”.

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As we shall show, there are many publications that appear to provide evidence in favour of a formate mechanism but in which it is clear that either a particular interpretation has been placed on limited and sometimes irrelevant experimental results, or the information is simply ambiguous and cannot be cited in support of any mechanism. We need to distinguish between what is known and what is not known!

It is certainly true that if the law of mass action applied to a reaction mechanism then the formate mechanism would be accepted for all catalysts under all experimental conditions. However, our own quantitative work [1–4] casts serious doubt on such conclusions and, recent theoretical calculations are almost unanimous in casting doubts on a formate mechanism because of the large activation barriers that are obtained in DFT calculations for such a mechanism [5–15]. While a recent comprehensive review on WGS [16] suggested that the DFT work may yet need to be refined by looking into the effect of co-adsorbed water on the decomposition of formates, it must be stressed that our own experimental work [1–4] was carried out under significant concentrations of water (e.g. 7%). In view of both our own work and this growing body of theoretical work that challenges a formate mechanism we believe it is timely to re-examine the evidence for and against a formate mechanism.

To provide clarity in this paper we will present the discussion of the relevant literature under the following headings:

- unambiguous quantitative evidence in support of a dominant formate mechanism on very low activity catalysts;
- unambiguous quantitative evidence against the “formate species detected by IR” being part of the main mechanism for high activity catalysts;
- the lack of quantitative evidence to support a formate mechanism on high activity catalysts;
- ambiguous experimental results that have been used to support a formate mechanism on high activity catalysts.

2. Unambiguous quantitative evidence in support of a dominant formate mechanism on very low activity catalysts

Tamaru and co-workers were the first to use a quantitative spectrokinetic method to investigate the water-gas shift reaction and discuss the possible relevance of IR-observable formates over unpromoted magnesia [17]. These authors used transmission FTIR with MgO wafers ($80\text{ m}^2\text{ g}^{-1}$). Formate species were observed on the magnesia surface after exposure to 5.3 kPa of carbon monoxide and 1.2 kPa of water in the IR cell. The pre-adsorption of formic acid on the wafer was used to draw a calibration curve between the IR band signal and the concentration of formate ions on the wafer. The surface concentration of formates was shown to be proportional to the absorbance of the C–H stretching mode band (measured in this work as O.D., “optical density”). These results are reproduced in Fig. 1, curve a.

The decay of the IR signal of the formate species at various temperatures in vacuum was followed for different initial surface coverages. A linear relationship was observed between the decomposition rate and the surface coverage as shown in Fig. 1, curve b. These observations indicate that the kinetics of formate decomposition followed a first order law, i.e. an exponential decay.

The specific rate of formate decomposition to CO_2 (in $\text{mm}^3\text{ g}^{-1}\text{ h}^{-1}$) was determined from the IR spectroscopic study of the surface and a gas-chromatography analysis of the products formed. This rate was compared to that of the water-gas shift reaction measured under experimental conditions yielding the same steady-state formate coverage and these two sets of results were

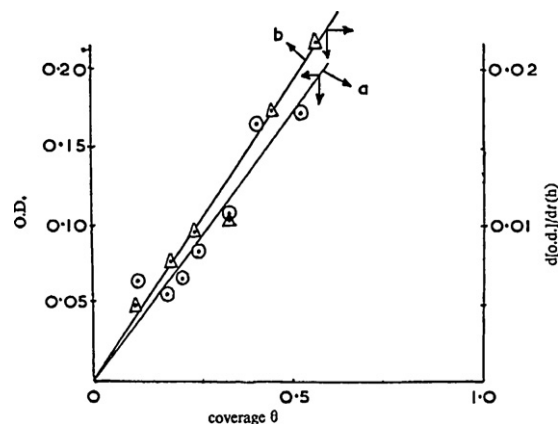


Fig. 1. (a) Correlation between the optical density (O.D. = absorbance) of the C–H stretching mode band and the coverage of formic acid on MgO. (b) Correlation between the decomposition rate of surface formate and its coverage on MgO. $T = 280^\circ\text{C}$.

(Adapted from reference [17] by permission of The Royal Society of Chemistry).

found to be close as shown in Table 1. Therefore, these results provided unambiguous evidence that the formates seen by IR could be main surface intermediates of the water-gas shift reaction. It must be stressed that this conclusion applies to a catalyst where the rate of the WGS reaction was extremely low, that is less than $0.4 \times 10^{-9}\text{ mol g}^{-1}\text{ s}^{-1}$ at 280°C .

Shido and Iwasawa in a highly cited contribution [18] have reported an in situ FTIR investigation of the reactivity of surface formates over a Rh/CeO₂ WGS catalyst. These authors were able to determine the selectivity in the decomposition pathways of surface formates, i.e. forward decomposition to $\text{CO}_2 + \text{H}_2$ and backward decomposition to CO and H_2O , using gas-chromatographic and mass spectrometric analyses. Importantly, formate species conversion to $\text{CO}_2 + \text{H}_2$ was dramatically improved in the presence of co-adsorbed water as compared to the case of a drier surface as shown in Fig. 2.

The WGS reaction rate was measured using a recirculating system and partial pressures of 4 kPa for CO and 0.67 kPa for water, that is with an unusually large CO:H₂O ratio. The specific concentration of formates over the very same sample was determined from temperature-programmed desorption analysis. The sum of the desorbed molar amounts of H₂ and CO was assumed to be equal to that of surface formates present under reaction conditions with H₂ being produced in the forward decomposition of formate and CO being produced in the backward decomposition of formate.

However, this method of quantifying the amount of formate on the surface is likely to overestimate the amount of formate on the surface at the end of the reaction. For example, the authors also showed that carbonate species were present and so some of the CO could have also come from the reaction of surface carbonate with ceria oxygen vacancies. In addition, CO disproportionation (i.e. the Boudouard reaction: $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$) can readily occur on Rh-promoted ceria [19,20] and even on plain ceria [21] which further complicates the analysis of the release of carbon monoxide

Table 1

Comparison between the rate of surface formate dehydrogenation and that of the water-gas shift reaction on MgO at 280°C , after reference [17].

Formate fractional surface coverage	Rate of formate decomposition to $\text{CO}_2 + \text{H}_2$ in $\text{mm}^3\text{ g}^{-1}\text{ h}^{-1}$	Rate of the water-gas shift reaction in $\text{mm}^3\text{ g}^{-1}\text{ h}^{-1}$ (in $\text{nmol g}^{-1}\text{ s}^{-1}$)
0.06	17	11 (0.14)
0.07	25	23 (0.29)
0.08	37	31 (0.38)

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