

in situ characterization of catalytic systems: differentiating actors and spectators for the water gas shift reaction on Pt and Au catalysts

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Introduction

Understanding the mechanism of catalytic reactions is a prerequisite to developing a logical approach to catalyst design. For this reason, experimental methods for investigating potential reaction intermediates have been developed over many decades. Spectroscopic techniques, particularly infrared spectroscopy, have been used extensively. However, in much early work there was no possibility to make simultaneous measurements of infrared spectra and reaction kinetics. The development of *in situ operando* techniques has provided the means to collect spectroscopic and kinetic data simultaneously. However, in many cases there is still a lack of a quantitative correlation between the concentration of surface species observed by infrared and the rate of reaction as measured online. This can result in serious errors in the interpretation of the results in terms of reaction mechanisms and the role of possible intermediates. The aim of this work is to present for the first time a fully quantitative analysis of the adsorbed species that are visible using infrared spectroscopy coupled with simultaneous measurements of the rate of reaction for the water gas shift reaction over platinum and gold catalysts. To further emphasize the importance of *in situ* correlations, results from some *in situ* EXAFS/XANES experiments on very high activity supported gold catalysts will be presented and discussed.

Materials and Methods

A commercial DRIFTS cell (Spectra-Tech[®]) was modified to ensure that there was no by-pass of the catalyst bed and that the characteristics of the cell were compatible with quality kinetic measurements. The original ceramic reactor was replaced with a custom-made ceramic reactor that was sealed with Teflon tape against the metallic support. Tests on the CO oxidation reaction showed that the by-pass was now negligible compared to more than 80% in the original commercial cell. The typical flow characteristics of the new cell were determined using a Kr tracer pulse and found to be nearly symmetrical with a mean value of ca. 6.8 s, a width of 3.5 s and an asymmetry of 2.2 s. The reaction rate for the water gas shift (WGS) reaction was measured using on line gas chromatography or mass spectrometry. Further experimental details can be found elsewhere [1-4].

Results and Discussion

The exchange of the gas phase reaction product CO₂ and that of formate surface species were followed during an isotopic exchange of the ¹²CO for ¹³CO at 160, 180 and 220 °C. The conversion of CO was determined to be 9, 23 and 39%, respectively. The data at 160 and 180°C showed that the exchange of the formates was significantly slower than that of the CO₂, clearly indicating that formates were unimportant at these temperatures. However, the exchange of formates and CO₂ occurred at a similar timescale at 220°C (Fig. 1, left). This apparent correlation between formates and the observation of labeled CO₂ in the gas phase based on these qualitative measurements was probed further by determining the absolute concentration of formate and correlating this with the rate of CO₂ formation measured by analyzing the effluent from the DRIFTS cell (Fig 1, right). These quantitative measurements clearly show that even though the fast formates exchange at 220°C at a rate

that is comparable to the rate of isotopic exchange of the product CO₂ the absolute amount of formate that is converted into CO₂ is very much smaller than the total amount of CO₂ produced.

The conclusion is that the DRIFTS-observable formates are minor reaction intermediates in the water gas shift reaction. The nature of the main reaction pathway, which could be a redox mechanism or a mechanism that involves an infrared-invisible species, will be discussed.

Significance

This research demonstrates the importance when using *in situ* infrared spectroscopy of making quantitative measurements of potential reaction intermediates. Without such analysis it is clearly possible to draw erroneous conclusions about the importance of various reaction intermediates. In the water gas shift example it is now clear for our catalysts, tested under our conditions, that formates are not the most important intermediate over a range of experimental conditions.

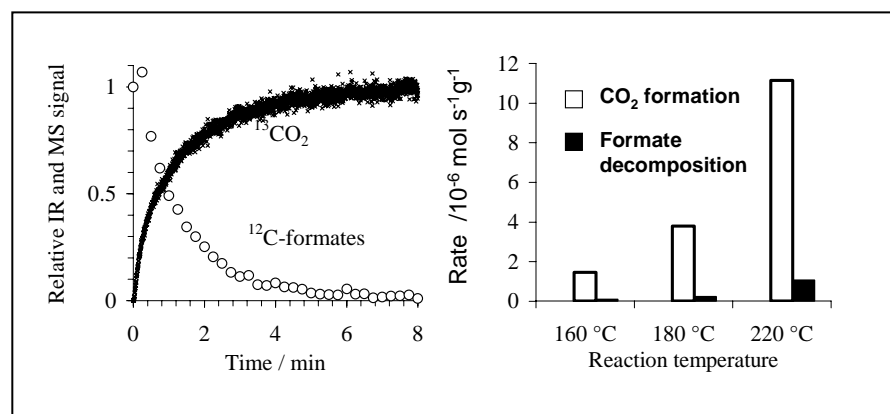


Figure 1. Left: Relative evolution of the intensity of ¹²C-containing formate (o) and ¹³CO₂ (x) signals with time on stream at 220 °C for a Pt/CeO₂ catalyst under 2% ¹³CO + 7 % H₂O, following steady-state reaction in 2% ¹²CO + 7% H₂O.

Right: Rate of CO₂ formation and rate of formate decomposition measured over the Pt/CeO₂ catalyst at three different temperatures. Feed is 2% CO + 7% H₂O.

References

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