

SSITKA-DRIFT analysis of the water-gas shift reaction on gold catalyst: elimination of formates seen by DRIFT as a key intermediate

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Introduction

The reactivity and the role of formate species on ceria-based water-gas shift (WGS, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) catalysts and the corresponding reaction mechanisms have been much debated [1-6]. Many of the conflicting conclusions are due to the fact that different materials and experimental conditions were used. In addition, a major source of discrepancy probably resides in the fact that the surface reactivity of adsorbates is often investigated using non-chemical-steady-state methods, leading to erroneous conclusions [6]. We show here how a combination of spectroscopic and kinetic data obtained at the chemical steady-state allows quantification of the concentration of reaction intermediates and excludes the role of the formate species that are visible by DRIFT.

Materials and Methods

The nature and reactivity of the formates and carbonates species formed at the surface of the 0.6 at.% Au/ Ce(La)Ox during the WGS were investigated using operando DRIFT spectroscopy during steady-state isotopic transient kinetic analyses (SSITKA). The preparation of the catalysts [1] and the details of the reactor, reaction gases and the SSITKA-DRIFT technique [6,7] have been reported elsewhere. The rate of CO_2 formation measured using the DRIFT cell in Belfast was identical to that measured in a quartz plug-flow reactor at Tufts University, indicating that the DRIFT cell behaved as a proper kinetic reactor. The DRIFT signal was used to quantify both the surface species and CO_2 relative concentrations. The absolute formate concentrations were determined using a calibration curve obtained from the analysis of standards prepared by impregnating sodium formate solutions over the support.

Results and Discussion

The exchange of the gas-phase reaction product CO_2 and that of formate and carbonate surface species were followed during an isotopic exchange of the reactant CO (i.e. switching from $^{12}\text{CO} + \text{H}_2\text{O}$ to $^{13}\text{CO} + \text{H}_2\text{O}$) at 155, 185 and 220°C; the CO conversion being 8, 15 and 25%, respectively. It is interesting to note that two types of reactivity were observed (see data at 185°C in Fig. 1, left). Some formates and carbonates exchanged on a timescale similar to that of the CO_2 , while a significant fraction exchanged at a much slower pace. The formate (and carbonate) exchange curves could be exactly deconvoluted into two single exponential contributions of “slow” and “fast” formates. The fast formates exchanged with a rate constant more than 10-fold higher than that of the slow species, while the fast formate proportion increased from ca. 40% at 155°C to ca. 70% at 220°C.

The specific rate of formate decomposition was calculated from the absolute formate concentration and the corresponding exchange rate constant and compared to the rate of CO_2

formation measured by analysing the DRIFT cell effluent (Fig. 1, right). The rate of formate decomposition was more than an order of magnitude lower than that of CO_2 formation, indicating that the DRIFT-observable formates were minor reaction intermediates or “buffer” species. The nature of the main reaction pathway (redox or based on IR-invisible adducts, not excluding formates) and the origin of the two-fold surface reactivity will be discussed.

Significance

This work shows unambiguously for the first time that the formates seen by DRIFT are not a main reaction intermediate species in the production of CO_2 in the present conditions over this catalyst, despite the fact that a fraction of those exchanged as fast as the reaction product CO_2 during a SSITKA analysis. This work demonstrates that it is critically important to quantify the IR data in order to obtain unambiguous mechanistic insights into the WGS reaction.

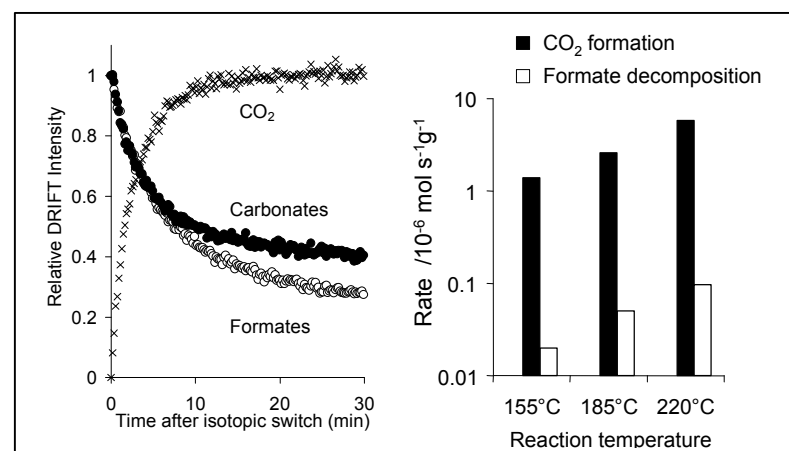


Figure 1. Left: relative evolution of the intensity of ^{12}C -containing carbonate band (●), ^{12}C -containing formate band (○) and $^{13}\text{CO}_2$ (x) signal with time on stream at 458 K under 2% $^{13}\text{CO} + 7\% \text{H}_2\text{O}$, following steady-state under 2% $^{12}\text{CO} + 7\% \text{H}_2\text{O}$. T = 185°C.

Right: Rate of CO_2 formation and rate of formate decomposition measured over the 0.6 at.% Au/ Ce(La)Ox catalyst at three different temperatures. Feed = 2% $\text{CO} + 7\% \text{H}_2\text{O}$

References

1. Fu, Q., Saltsburg, H., Flytzani-Stephanopoulos, M. *Science* 301, 935 (2003).
2. Luo, T., Gorte, R.J. *Catal. Lett.* 85, 139 (2003).
3. G. Jacobs, B.H. Davis, B.H. et al. *Catal.Today* 106, 259 (2005).
4. Leppelt, R., Schumacher, B., Plzak, V., Kinne, M., Behm, R.J. *J. Catal.* 244,137 (2006).
5. Kim, C.H., Thompson, L.T., *J.Catal.* 230, 66 (2005).
6. Tibiletti, D., Goguet, A., Meunier, F., Breen, J., Burch, R. *Chem. Comm.* 1636 (2004).
7. Meunier, F.C. et al., *J. Catal.* 244, 183 (2006).