# Pulse-Response TAP Studies of the Water-Gas-Shift Reaction over a Pt/CeO$_2$ Catalyst

S.O. Shekhtman*, A. Goguet, R. Burch, C. Hardacre, N. Maguire

CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast,
Belfast BT9 5AG, UK,
* s.shekhtman@qub.ac.uk

Introduction

The development of hydrogen fuel cells is amongst the most promising of all the future energy solutions providing efficient power with little environmental impact. However, providing hydrogen in a form which has sufficient purity not to deactivate the fuel cell is a major challenge. The reforming of hydrogen-rich fuels, including from renewable sources, is an option with great potential. Such reforming process involves a catalytic Water Gas Shift step (WGS) which converts water into hydrogen whilst also removing carbon monoxide, a poison for the fuel cell, forming carbon dioxide:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
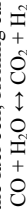
Recent studies have shown that noble metals (e.g. Pt, Au) supported on CeO$_2$ are promising low-temperature catalysts for this reaction. However, the literature contains conflicting reaction mechanisms by which the WGS reaction proceeds [1, 2].

Over the last two decades, the Temporal Analysis of Products (TAP) technique [3] has been successfully applied to non-steady-state kinetic characterization of model and multicomponent industrial catalysts in many areas of chemical kinetics and engineering. This paper demonstrates for the first time that the TAP technique can be applied to the WGS reversible reaction in order to provide unique information concerning the nature and reactivity of key surface intermediates that may be relevant to the reaction mechanism for a 2%Pt/CeO$_2$ catalyst. Herein, the reaction between the specific gas reactants and a catalyst that has been conditioned to have a particular surface composition has been measured to identify separate elementary steps of the reaction mechanism

Materials and Methods

The catalyst used in this study was a 2%Pt/CeO$_2$ provided by Johnson Matthey plc. The TAP pulse-response experiments were performed in a TAP-I apparatus using a stainless steel microreactor (41 mm long and 5.5 mm inner diameter). In all experiments, the thin-zone TAP reactor was used: it was packed with two 17 mm long beds of silicon carbide sandwiching 1 mm of catalyst. Reactants and products were recorded at the reactor outlet by a UTI 100C quadrupole mass spectrometer.

Results and Discussion

For the forward water gas shift reaction, it was found that the variety of different catalyst compositions generated in the CO multi-pulse TAP experiment over the catalyst pre-treated using four different normal pressure flows (containing O$_2$, H$_2$O, CO$_2$ or H$_2$) can be described using one general scale, based on the amount of consumed CO using the final CO-saturated catalyst composition as the aligning point. The influence of different pre-treatments, which appears as different starting points, was quantified in terms of the amount of CO molecules consumed by the catalyst.

From the kinetic analysis of the CO multi-pulse responses, two kinetic regimes and correspondingly two kinds of active sites involved were identified. The numbers of these active sites and their intrinsic parameters were determined. The influence of the temperature was described quantitatively:

- The amount of more active sites does not change significantly (remains around 1.35*10^{-7} mole/mg) while the amount of less active sites increases with temperature.
- The activity of both kinds of active sites follows Arrehnius dependence.

At 250 and 300C, the amount of CO$_2$ produced over O$_2$, H$_2$O and CO$_2$ pre-treated catalysts was found to be much smaller than the observed CO consumption indicating a small contribution of the redox mechanism. The major amount of CO was consumed in a form of surface intermediate more stable than the intermediates formed when CO$_2$ was pulsed over CO$_2$ pre-treated catalyst. This agrees with the proposed associative mechanism and explains remarkable agreement between the determined amounts of two kinds of active sites and the amounts of gaseous CO and CO$_2$ released by the catalyst surface after isotope switch observed in the SSITKA experiment under normal pressure reaction conditions at 225C (2.2*10^{-7} mole/mg and 8.4*10^{-7} mole/mg) [1].

For the reverse water gas shift (RWGS) reaction, the adsorption/desorption rate constants for CO$_2$ and H$_2$ have been determined in separate TAP pulse response experiments and the amount of H-containing exchangeable species has been determined using D$_2$ multi-pulse TAP experiments. This number is similar to the amount of CO precursor observed in previous SSITKA experiments [1]. The CO production in the RWGS reaction was studied in a TAP experiment using separate and consecutive pulsing of small amount of CO$_2$ and H$_2$. The dependence of CO yield on CO$_2$ and H$_2$ pulse intensities as well as on the time delay between CO$_2$ and H$_2$ pulses was determined. A small CO yield was observed when CO$_2$ was pulsed alone over the reduced catalyst. When H$_2$ pulses were added, CO yield increased significantly with the intensity of H$_2$ pulse. In terms of pulse sequence, the maximum CO yield was observed when the CO$_2$ pulse was followed by a H$_2$ pulse with 1 s delay. Based on these findings, it was concluded that an associative reaction mechanism dominates the RWGS reaction under the vacuum TAP experiment conditions. The proposed reaction mechanism includes: fast adsorption of CO$_2$ (primarily on ceria) and H$_2$ (dissociative, primarily on platinum), slow formation of a reactive carbon containing intermediate, fast reaction of this intermediate with adsorbed hydrogen forming adsorbed CO and OH group and finally release of adsorbed CO and water. From the TAP data the rate constants for several elementary steps were determined [2].

Significance

We demonstrate how the TAP technique provides unique kinetic & mechanistic information when applied for the first time to **reversible** WGS reaction which is important for H$_2$ fuel cells.

References

1. Goguet, A., Tibiletti, D., Meunier, F.C., Breen, J.P., and Burch, R. *J. Phys. Chem.* B, 108, 20240 (2004)
2. Goguet, A., Shekhtman, S.O., Burch, R., Hardacre, C., Meunier, F.C., and Yablonsky, G.S. *J. Catal.*, 237, 102. (2006)
3. Gleaves, J.T., Yablonsky, G.S., Phanawadee, P., and Schuurman, Y. Appl. Catal. A, 160 55 (1997).