Insights into the low temperature activity of gold based catalysts for water gas shift using plasma

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Abstract: Plasma-assisted water gas shift reaction over a Au/$CeZrO_4$ catalyst at low temperature has been investigated. The activity obtained was comparable with that attained by heating the catalyst to ~180 ^{o}C providing an opportunity for the hydrogen production to be obtained under conditions where the thermodynamic limitations are minimal. The *in-situ* DRIFTS analysis reveals the structural changes associated with the gold nanoparticles in the catalyst have been observed which are not found under thermal activation indicating a weakening of the Au-CO bond and a change in the mechanism of deactivation.

Keywords: Au catalyst, WGS, Non-thermal plasma

1. Introduction

Many reversible exothermic reactions are of great industrial importance. For instance, the water gas shift (WGS) reaction is a key step in the production of clean hydrogen for processes such as oil refining, ammonia synthesis or hydrogen fuel cells. The main role of this reaction step is to remove the CO formed during the upstream hydrocarbon reforming reactions while increasing the hydrogen yield. This process is essential since CO is usually a poison for downstream processing catalysts. Combining heterogeneous catalysts with non-thermal plasmas (NTP) proves to be a powerful tool for promoting reactions to occur at ambient operational temperatures but it is, equally, very difficult to understand. This is mainly due to the lack of *in situ* measurements that would allow a better understanding of reaction mechanisms by identifying the active site, reaction intermediates and probing the intrinsic kinetics of the reaction for a working catalyst under realistic plasma conditions.

This study aimed to combine a powerful *in situ* technique, diffuse reflectance infra-red spectroscopy (DRIFTS) with DFT calculations to study the effect of plasma on the catalyst, particularly on the gold sites.

2. Experimental

In situ DRIFTS [1] was used to probe the gold active site under the NTP activation and compare that with thermally activated catalyst. Au/CeZrO4 catalyst was loaded into the IR cell and pre-treated at 150 °C for 30 min under Ar to ensure any residual water was removed from the catalyst before being exposed to the plasma. The temperature was then decreased to room temperature and the NTP was generated in close contact with the surface of the catalyst. The simplified forward WGS feed was allowed to flow through the T-shape quartz tube to the plasma region and exit the cell through the catalyst bed. The power electrode was driven at a peak voltage of 6.0 kV and the pulse frequency was kept at 22.0 kHz to avoid arcing between the external electrode and the collector. IR spectra were recorded every 60 s with a resolution of 4 cm^{-1} and were analyzed with the OPUS software.

All the DFT calculations were carried out with a periodic slab model using the Vienna *ab initio* simulation program (VASP) [2]. To decompose the effect of plasma, we only considered the metallic gold surfaces in our DFT calculations. The Au(111) and Au(100) were chosen as the model surfaces for water gas shift.

3. Results and discussion

In-situ DRIFTS coupled with NTP activation has led to the formation of various types of both gas phase and surface species that are reported to be formed under various WGS conditions over different catalyst. It is seen in Figure 1 that NTP has an influence on the nature of CO adsorbed species. The region where CO is adsorbed has been shown to be extremely valuable in identifying the Au species present under reaction conditions. For the thermal activation at 150 °C, it is found that the majority of Au^0-CO species are present with an adsorption band at 2095 cm^{-1}. Also, there is a small contribution of $Au^{\delta+}$-CO species at 2120 cm^{-1}. However, there are significant changes in the CO during the NTP on/off switches. According to Figure 1 and during the first cycle, it is very clear that, with NTP on, both Au^0-CO and $Au^{\delta+}$-CO species are detected and the Au^0-CO species are more dominant than the $Au^{\delta+}$-CO species. Once the NTP is switched off for the first cycle, the significant change in Au^0-CO species is observed in which its intensity is decreased dramatically while the $Au^{\delta+}$-CO species slightly change. It is interesting to point out that, when the plasma is switched on for each cycle, the Au^0-CO species decrease whereas the $Au^{\delta+}$-CO species increase from one cycle to the next. The same trend is observed for both Au species when the plasma is switched off for each cycle but with only $Au^{\delta+}$-CO species are predominant. There is clear evidence that the DBD affects the structural properties of the gold leading to a significant change in the adsorption properties of CO indicative of a weakening of the Au-CO bond.

In addition to DRIFTS study, the preliminary DFT studies indicate that the low temperature activity could be due to water activation by the plasma prior to the adsorption on the surface through the formation of species such as OH and H_2O^+ both of which have been observed under plasma conditions in the gas phase.

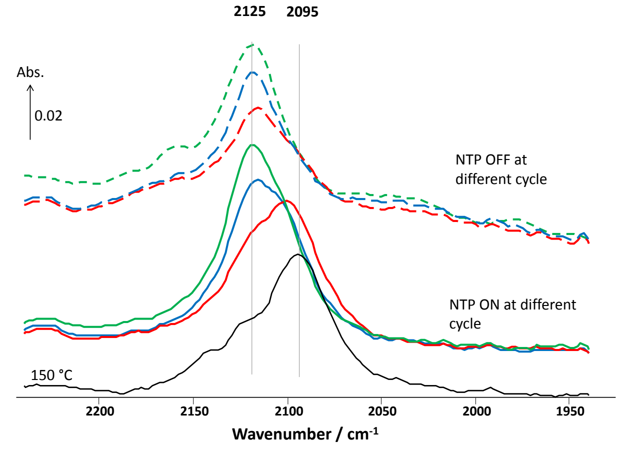

Figure 1. The effect of NTP-catalyst system on the CO conversion: DRIFT spectra.

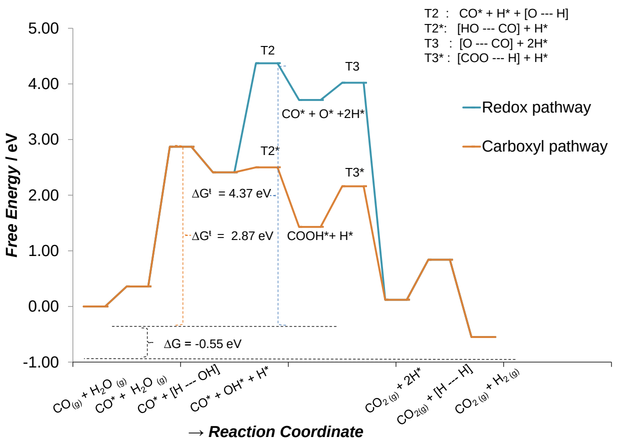

Figure 2. Free energy profile of WGS on Au(111) for both redox and carboxyl pathways.

4. Conclusions

Under plasma control, the gas phase molecules are activated at low temperature providing an alternative route for the reaction and allowing significant reaction under ambient temperature conditions for the first time. *In-situ* diffuse reflectance infra-red spectroscopy coupled with NTP activation lead to the formation of various types of both gas phase and surface species including CO (ads), CO_2 (g and ads), formates, carbonates and water that have been previously reported for thermally conducted reactions. The combination of the plasma with a high activity thermal catalyst provides a significant technological advance in the production of clean hydrogen at low temperatures.

References

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