Study of Au/$CeZrO_4$ catalysts for the low temperature Water Gas Shift reaction; identification of the active Au species

H. Daly, F. C. Meunier[†], R. Pilasombat, R. Burch, A. Goguet* and C. Hardacre
CenTACat, Queen's University Belfast, Belfast BT9 5AG, U.K.
* a.goguet@qub.ac.uk
[†]Current address: LCS, Univ. Caen, CNRS, 6 Bd Maréchal Juin, F-14050 Caen, France.

Introduction

The importance of the preparation method of gold-oxide supported catalysts in achieving highly active catalysts for reactions such as WGS is widely known. Au supported on $CeZrO_4$ has been found to be one of the most active catalysts for the WGS reaction [1] although there is still an issue with the stability of these catalysts which is hindering their practical application. While there is an understanding of how to produce active catalysts for the WGS reaction there is no consensus on the nature of the active Au with positively charged [2] and metallic gold [3] all proposed to be the active state of the gold.

Infrared spectroscopy has been widely employed to characterise the state of the Au through analysis of the Au-CO band position and in this study, we have carried out an in-situ DRIFTS-GC analysis of 1%Au/$CeZrO_4$ for the WGS reaction. We have investigated the deactivation of the catalyst due to elevated reaction temperature and the amount of water in the feed and studied the evolution of the Au-CO bands during the reaction to assess the nature of the active Au.

Materials and Methods

1% Au/$CeZrO_4$ catalyst was prepared using a deposition precipitation (DP) method with vacuum drying of the precipitate. The long term stability of the catalysts at 150°C under the WGS feed (2.0%CO, 2.5%CO_2, 8.1%H_2 and 7.5%H_2O) was studied in a microreactor with on line GC analysis of reactants and products. The deactivation of the catalysts was also studied under the same WGS reaction conditions in a DRIFTS-GC setup which consisted of an in-situ high temperature diffuse reflectance IR cell (Spectra-Tech) fitted with ZnSe windows; the cell has been modified in house to behave as a plug flow reactor [4] and holds 50±5mg of catalyst. All spectra have been referenced to the fresh catalyst under Ar and have been corrected for gas-phase CO and the band due to the normally forbidden electronic transition of partly reduced ceria [5]. The deactivation of the catalyst was investigated under normal WGS conditions at 150°C and also at an elevated reaction temperature of 400°C and under lower water content feed (1% H_2O). Spectra were recorded for a total of 20 hours on stream and the evolution of the Au-CO bands monitored.

Results and Discussion

The Au species identified on the catalyst under the WGS feed at 150°C are assigned to Au^0-CO, band observed at 2095 - 2100 cm^{-1}, $Au^{\delta+}$ at 2125 cm^{-1} (shoulder on main band) and $Au^{\delta-}$ at 2050-1965 cm^{-1} [6]. As the catalyst deactivates, there is a decrease in the Au-CO bands with loss of the $Au^{\delta+}$-CO bands at a faster rate than the Au^0-CO bands. However, the catalyst is still active when there is no $Au^{\delta+}$-CO bands observed. $Au^{\delta+}$ species are reduced under the feed and are not the active species for the WGS reaction

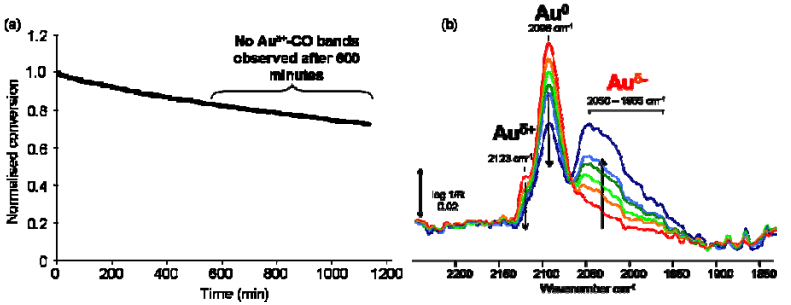

Figure 1: DRIFTS spectra of 1% Au/$CeZrO_4$ under the WGS feed (7.5% H_2O) at 150°C (a) normalized conversion and (b) evolution of Au-CO band intensity with time on stream.

With time on stream, $Au^{\delta-}$-CO bands are observed to increase at ~2050 – 1965 cm^{-1}. These Au species are increasing while the catalyst is still deactivating so these species cannot be active for the WGS reaction. The change in the Au^0-CO band correlates with the deactivation rate of the catalyst under the different WGS feeds.

The same trend regarding changes to the Au-CO bands is observed under the 1% water feed except the change in the Au^0-CO band is slower in line with the slower deactivation. The changes to the Au-CO bands are more dramatic following reaction at 400°. After 1 hour at 400°C, the activity has halved and there is a corresponding decrease in the Au^0-CO band intensity. $Au^{\delta+}$-CO bands are fully depleted during the treatment at 400°C. The subsequent rate of change in the Au^0-CO bands further maps the deactivation with time on stream. Interestingly, no $Au^{\delta-}$-CO bands form following reaction at 400°C.

Significance

Investigation of the deactivation of a 1%Au/$CeZrO_4$ catalyst using in-situ DRIFTS-GC allowed clarifying the role of Au^0, $Au^{\delta+}$ and $Au^{\delta-}$ species in Au/$CeZrO_4$ low temperature WGS catalysts. $Au^{\delta+}$ and $Au^{\delta-}$ could be discarded as possible active sites while the results are consistent with metallic gold being the active Au species

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